TANNING MATERIALS

WITH NOTES ON

TANNING EXTRACT MANUFACTURE

BY

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PRACTICAL LEATHER CHEMISTRY

A Handbook of Laboratory Notes and Methods for the Use of Students and Works Chemists

PREFACE

THE lack of a book dealing with the composition of the more important Tanning Materials has prompted the writer to present this volume. As is well known, information concerning those materials used for vegetable tanning is widely disseminated through a number of publications, many of which are inaccessible to the average tanner or manufacturer, and it was considered that if such information was brought within the scope of a single volume, it would form a useful book of reference to those interested. This, at all events, is the anticipation of the author, and if such is realised, the work involved in bringing the subject matter together will be amply rewarded.

Section II. has been so arranged that the tanning materials are discussed in alphabetical order, thus making it in the nature of a dictionary of the subject. This will doubtless appeal to the majority, in view of its convenience for reference purposes.

Naturally, no book on tanning materials would be complete without some reference to tanning extracts, the manufacture of which is dealt with in Section III., as well as being mentioned throughout Section II. This, of course, is a very specialised subject, and one upon which a separate volume might well be written. It is hoped, however, that the details given will be both useful to the manufacturer and interesting to the student of the leather trade, who will want to know at least an idea of the method of manufacture of these widely used materials.

Section IV. contains the official methods of analysing tanning materials, as laid down by the Society of Leather Trade Chemists and the American Leather Chemists Association.

The author desires to express his indebtedness to those gentlemen who have so freely offered suggestions in connection with this volume, more especially Mr J. A. Reavell, M.I.M.E., and Mr W. A. Fraymouth, F.C.S. Best thanks are also due to the Forestal Land, Timber, and Railways Co. Ltd., The Kestner Evaporator and Engineering Co. Ltd., and many other manufacturers for the loan of the blocks which have been used to illustrate the text.

A. H.

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Calculation of Material for Extract Making.

IN the manufacture of tanning or wood extracts it is customary to calculate the approximate amount of raw material which will be required to produce a given amount of finished extract in order that any possible losses can be traced.

In this connection an article by Eitner in *Der Gerber*, 1907, is of particular interest. This article, containing much practical information, was abstracted in *Jour. Amer. Leather Chem. Assoc.*, 1907, from which the following notes have been compiled.

Talking of pine barks, he says that one observation made was that on extraction a considerable amount of tannin totally disappears and cannot be accounted for in the extract produced. In support of this statement, the following examples are given :—

1. Pine bark extracted in a tannery in a battery of six leaches, boiling in the last leach.

			Per Cent.
Total extractable matter of the new bark, air dry	-	-	24.8
" " in the obtained liquor	-	9.41	
" " in the spent bark	-	9.28	
Extraction obtained	-		18.69
Loss	-	-	6.11

24.5 per cent. of the total extractable matter.

2. Pine bark extracted in an extract works by entirely hot extraction.

			Per Cent.
Total extractable matter in the air dry bark	-	-	24.36
" " in the obtained liquor	-	12.9	
" " in the spent bark	-	6.36	
Extraction obtained			19.26
Loss	-	-	5.10

20.9 per cent of the total extractable matter.

3. Pine bark extracted by the author in a battery of six leaches, boiling in the last leach, the others being treated cold.

			Per Cent.
Total extractable matter	in the dry bark		28.96
" "	in the obtained liquor	11.55	
" "	in the dry spent bark	10.56	
Extraction obtained			22.11
Loss			6.85

26.8 per cent. of the total extractable matter.

4. Pine bark extracted entirely by hot extraction.

			Per Cent.
Total extractable matter	in the air dry bark		24.33
" "	in the obtained liquor	11.85	
" "	in the spent bark	8.36	
Extraction obtained			20.21
Loss			4.12

20.8 per cent. of the total extractable matter.

5. Oak wood extracted hot in open leaches.

			Per Cent.
Total extractable matter	in the air dry wood		12.8
" "	in the obtained liquor	7.12	
" "	in the spent bark	1.10	
Extraction obtained			8.22
Loss			4.6

36 per cent. of the total extractable matter.

6. Quebracho wood extracted in hot diffusers.

			Per Cent.
Total extractable matter	in the new wood		24.68
" "	in the obtained liquor	17.29	
" "	in the spent wood	1.98	
Extraction obtained			19.27
Loss			5.41

22.3 per cent. of the total extractable matter.

It will be observed, therefore, that the loss is considerable, and a possible reason should be forthcoming.

It is the opinion of the present writer that such loss results from the combined causes of decomposition of tannin and the precipitation of difficultly soluble tannins in the vat, mostly the latter. At the dilution which is used in the analysis of the bark, such difficultly soluble matter remains in

solution, but at the higher concentration of the vat, liquor comes down in the form of a precipitate, and settles out as a sludge.

Also it is recalled that in the extraction of materials in a series of leaches, the temperature of the liquor running over the leach containing new bark is comparatively low, and the cooling effect on the liquor, containing, say, 9-10 per cent. of solids, would be to cause the precipitation of any difficultly soluble matter. This might possibly explain the apparent loss which takes place. In settling and cooling prior to concentration, there is also a precipitation of some tannin-like substances. It will be noted in Eitner's figures only the loss in total extractable matter is given, and one might be led to think that this is mainly non-tannin substances. Such, however, is not the case, as the writer is in possession of facts which show that there is, in what is known to be a good system of extraction, a loss of tannin substance which cannot be accounted for when investigation is made of the liquor and spent bark. The question of precipitation of difficultly soluble matter being the cause of the loss mentioned above is discussed by Eitner (*loc. cit.*), who comes to practically the same conclusions as the writer. In the abstract referred to the following note is made on this point.

In practice the materials are leached hot, and are cooled off before use, whereby the sediment settles out, and as this contains substances which are reported in the analysis as tannin, it is evident that part of the loss in leaching can be found here. The pine bark (4) mentioned earlier has been used by Eitner to determine the loss in sediment, and as they represent results of some valuable work, they are quoted *in extenso*.

The dust-free bark was used and extracted at different temperatures, and the amounts of total soluble matter, spent tan, and sediment determined.

PINE BARK—EXTRACTION EXPERIMENTS.

Temperature.	Sediment.	Extractable Matter in Sediment.
	Per Cent.	Per Cent.
20	1.26	0.36
40	4.21	1.40
70	7.40	5.12
100	9.46	5.48

Taking into consideration the soluble matter present in the sediment it will be seen from the series of figures given herewith that the loss formerly mentioned is partly accounted for.

EXTRACTION AT 20° C.

		Per Cent.
Total extractable matter in the bark		24.33
" " in the liquor	8.54	
" " in the sediment	0.36	
" " in the spent bark	14.28	
		23.18
Loss		1.15

4.61 per cent. of the total extractable matter.

EXTRACTION AT 40° C.

		Per Cent.
Total extractable matter in the bark		24.33
" " in the liquor	9.34	
" " in the sediment	1.40	
" " in the spent bark	10.54	
		21.28
Loss		3.05

12.5 per cent. of the total extractable matter.

EXTRACTION AT 70° C.

		Per Cent.
Total extractable matter in the bark		24.33
" " in the liquor	10.67	
" " in the sediment	5.12	
" " in the spent bark	6.34	
		22.13
Loss		2.20

11.9 per cent. of the total extractable matter.

EXTRACTION AT 100° C.

		Per Cent.
Total extractable matter in the bark		24.33
" " in the liquor	11.04	
" " in the sediment	5.98	
" " in the spent bark	4.01	
		21.03
Loss		3.30

13.5 per cent. of the total extractable matter.

Even now it will be seen that some serious losses seem unaccounted for, but if, as is afterwards done, the whole of the sediment is included in the above figures, the total will come to very near the theoretical amount.

Looking over all the tables quoted, it is clear that an analysis of a material is somewhat misleading when used for calculating out quantities required for extract making, and such should be borne in mind by both tanners who make their own extract and also by extract manufacturers.

To illustrate this loss in practice, an example which came to the notice of the present writer will be quoted.

The bark used in the factory had the following composition:—

	Per Cent.
Tannin	16.0
Soluble non-tannins	6.0
Insoluble matter	28.0
Moisture	50.0
	100.0

and the extract is made so that the tannin content is 55 per cent. Now, the theoretical amount of bark required to make 1 cwt. of 55 per cent. extract is about 385 lbs., and yet in practice one has to use from 455-460 lbs. Thus there is a surplus of 75 lbs. of bark required per cwt. of extract, or an apparent loss of 12 lbs. of tannin per cwt. extract.

The loss is no doubt due to formation of sludge consisting of difficultly soluble tannins, and, of course, when decolorising is carried out with such materials as albumin, there will be a loss of tannin here which will all tend to lower the yield of extract of a definite tannin strength.

Spent Bark as Boiler Fuel, etc.

At most extract factories, it is the practice to make use of the spent material from the extractors as boiler fuel. The value of this material as fuel depends upon its calorific value, and also on the degree of disintegration that has been applied to the original raw material. In the case, however, of chestnut chips from an extract factory, it may be taken that the chips contain about 65 per cent. of moisture as they come from the extractors, and about 35 per cent. of woody fibre. The calorific value of the woody fibre itself is about half that of coal, whilst the moisture has to be evaporated off before the fuel is of value. It is obvious that in order to get steaming

results from the boilers in using this class of fuel, the ratio of grate area to heating surface must be greatly increased.

Many different devices are adopted in connection with the burning of spent material from extract factories, and it is usual to eliminate some of the moisture from the spent material before using it in the boiler furnaces. For fibrous materials such as barks it is common practice to pass the spent bark through tan presses or heavy iron mangles, and it may be accepted that such a method of treatment of the spent material containing 65 per cent. of moisture, as it comes from the extractors, reduces the moisture to 45-50 per cent.

Recently an ingenious centrifugal arrangement has been introduced, termed a "Continuous Centrifugal," and on experiments conducted with sumach leaves, containing so much fluid as to be easily pumped in a rotary pump, with a moisture percentage on the solids of over 200 per cent., a 24-in. machine, running at 1,200 revs. per minute, reduced the moisture to 27 per cent. in 300-400 gals. per minute of pulp, which made this difficult class of waste material suitable for firing in the boilers. The construction of this machine is an outer centrifugal basket with perforations, revolving with an inner closed centrifugal at a lower speed. The surface of the latter is grooved, so that the material, while it is being revolved in the centrifugal basket, is gradually pressed forward between the two revolving baskets, so that the delivery of the spent material, after the moisture is extracted, is continuous. When this continuous centrifugal is perfected and put in the market, its uses will be of great advantage in extract factories dealing with waste spent material for boiler purposes.

The systems adopted for burning this waste material are briefly as follows:—

Gas generator or destructor furnaces, built externally to the boilers, and so arranged that the heated gases pass by a duct to the heating surfaces of the boilers. Those furnaces are generally of the flat grate type and fed by hoppers overhead. Cleaning doors are provided at even distances along the sides of the furnaces. It is a general practice to provide forced draught for this class of furnace, which can either be of the fan or steam-jet air-blast type.

The step grate furnaces are also very frequently used at extract factories, and are particularly adapted for water-tube boilers. The inclined grates are so graded that the fuel will readily fall down the grate, as it is fed from the hopper at the top of the furnace. Ample fire-brick arching is provided in

these furnaces, the idea being that the reflected heat from the arches over the furnace gives a rapid evaporation to the moisture in the fuel, so that when it descends on the step grate, it reaches incandescence, and performs its functions as boiler fuel.

The Godillot furnace is a modification of the step grate furnace. It is constructed in the form of a half section cone, and is described as a pavilion grate. The fuel to be burned is put into a charging hopper, where a worm feed delivers it to the apex of the pavilion grate, where it drys, heats, inflames, and descends on the grate bars in the form of a thin layer, in proportion as the fuel underneath is consumed. Finally, it reaches the horizontal grate, where combustion is finished, and the ashes drawn out as required.

A fair estimate as to the value of wet spent tans, containing 60 per cent. of moisture, would be a consumption of about 50 lbs. of fuel per square foot of grate area per hour, and it would be expected that 1 lb. of this class of fuel would evaporate about 1.5 lbs. of water with natural draught, and with forced draught with, say, 1½ in. of water gauge in the ash pit, the evaporation would be in the neighbourhood of 1.75 lbs. per lb. of fuel.

In order to successfully burn spent material from an extract factory in the boilers, each class of fuel and conditions pertaining thereto would have to be studied separately, but in a well regulated extract factory, practically all the fuel used should be available from the waste material from the extractors.

Distillation of Wood.

As is well known, wood when destructively distilled yields, among other products, methyl alcohol, acetone, acetic acid, and a tarry mixture, leaving in the retort wood charcoal. During decomposition, gases are evolved, the composition of which varies with the temperature at which the distillation is carried out. Such gases, after appropriate treatment, can be used for heating purposes.

To ascertain whether it might be a profitable proposition to distil tan waste, some experiments are being carried out by the present author. In one test, spent mimosa bark yielded on distillation an aqueous liquor at the rate of $3\frac{1}{8}$ gals. per 100 lbs. air dry material, the acidity of which corresponded to 2 per cent. of acetic acid; calculated on the weight of spent bark. This is equivalent to about 2½ per cent.

lcium acetate, and is a low yield as compared with some oods which are commonly used for distillation purposes. Red oak, quoted by Hubbard ("Utilisation of Wood Waste," p. 72), gives a yield varying from 3.84-5 15 per cent., according to the method of treatment.

Pine wood, distilled at the Imperial Institute, yielded 2.9 per cent. of calcium acetate.

Judging from the one experiment (which, of course, is not conclusive), it would not be profitable to distil the spent bark for the sake of the acid produced. However, the other products formed have to be considered, and as experimental work has not advanced to this stage, the writer can give no definite details.

Some interesting details on the distillation of wattle wood are given by the Imperial Institute (Bulletin, 1916, p. 556 *et seq.*). This wood accumulates as a by-product in the Natal wattle bark industry, and it was considered possible that use might be made of it in the manufacture of wood alcohol, acetic acid, etc. The results obtained are given below for reference, together with those for other woods examined at the same time:—

	Black Wattle.	Olive Wood.	Pine Wood.	Oak Wood.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Acetic acid	4.7	3.0	2.2	4.4
Methyl alcohol	1.2	1.6	0.6	1.1
Tar (separated)	6.0	7.4	12.9	6.4
Charcoal	27	29	29	25

The total value of the products obtained from one ton of black wattle wood was £2. 7s. 5d., based on 1914 values.

Paper-Making.

The question of paper-making from spent barks has already been alluded to, and the work carried out at the Imperial Institute has given most interesting and valuable results. This work was confined to wattle bark, and it is shown (Bulletin, 1917, p. 509) that by appropriate treatment with caustic soda under pressure, the bark can be made to yield a pulp which can subsequently be bleached to a cream colour. The yield of dry unbleached paper is from 28-35 per cent. on the weight of spent bark. Manufacturers' trials

gave a yield of 28-30 per cent. of pulp considered suitable for brown paper making. The 34 per cent. yield of unbleached paper was obtained by heating the bark for four hours at 140° C. with a caustic lye containing 20 parts of caustic soda per 100 of bark used.

Mordanting Value of Tannin.

In addition to the leather trade, the tannin-bearing materials and the extracts prepared therefrom are widely used as mordanting agents in the textile trades. Cloth so mordanted takes up certain dyes more readily than unmordanted material.

In this connection, Wisdom (*Jour. Amer. Leather Chem. Assoc.*, 1919, p. 6) has investigated the relative mordanting value of a number of common tanning materials. When cotton cloth is soaked in a 0.4 per cent. tannin solution at a temperature of 160° F. and then shaken for one hour, the following amounts of total soluble matter are absorbed, varying with the tanning material used :—

Material.	Per Cent. absorbed calculated on the Tannin Percentage of the Material.
Galls	25.3
Sumach	27.3
Myrobalams	22.3
Divi-divi	18.1
Quebracho	17.3

This, however, does not represent the amount of tannin absorbed by the fabric, but the non-tannins and tannin together. To obtain some idea of the actual mordanting value of the tannins, cloth was treated with the various tannin solutions, washed out and then immersed in an iron liquor. The dried cloth was then ashed and the amount of iron fixed by the tannin estimated. Each 100 parts of tannin matter absorbed fixed the following amount of iron oxide, Fe_2O_3 :—

Material.	Per Cent. absorbed calculated on the Tannin Percentage of the Material.
Galls	36.5
Sumach	33.5
Myrobalams	34.5
Divi-divi	32.4
Quebracho	24.4

By multiplying the absorption figure by the iron combin-

ing figure and calculating them to a percentage of the tannin in the material used for mordanting, the so-termed "mordanting value" is arrived at, which for pure extracts should approximate to the following, using galls as the standard at 100:

Material.	Per Cent. absorbed calculated on the Tannin Percentage of the Material.
Galls	100.0
Sumach	87.4
Myrobalams	72.6
Divi-divi	59.3

In view of the fact that cutch is so widely used as a dyeing and mordanting material for boat sails, it is unfortunate that this substance was not examined on the same lines, more especially as this is the only material which can satisfactorily be used for this purpose, and some characteristic feature might have been discovered.

Logwood.

Although used for dyeing purposes, logwood is so closely associated with the leather trade that a few remarks concerning the material will not be out of place.

Logwood of commerce is obtained from the tree *Hæmatoxylon campechianum*, and constitutes the raw material for the manufacture of logwood extract.

Some analyses of genuine Jamaica wood are given by Vie (*Le Cuir*) as follows:—

	Per Cent.	Per Cent.
Moisture	17.50	19.39
Tannin	6.92	7.11
Soluble non-tannins	5.03	5.60

These are similar to an analysis of what is termed bastard logwood, sometimes called mulatto logwood, examined by Drabble and Nierenstein.

	Per Cent.
Tannin	6.34
Soluble non-tannins	4.50
Insoluble matter	79.44
Moisture	9.72

In passing, it is of interest to note that this latter material

contains little or no dyestuff, and the tannin present belongs to the catechol group.

According to Vie, the composition of logwood extract is represented as under:—

	Per Cent.	Per Cent.	Per Cent.
Insoluble matter	0.25	0.19	0.23
Soluble matter	44.52	39.97	41.67
Tannin	23.70	20.84	21.32
Soluble non-tannins	20.82	19.13	20.35

Although not much in practice at the present time, it is said that logwood extracts were very liable to adulteration with either chestnut extract or molasses.

In the extraction of logwood for the preparation of extract, it is necessary to allow oxidation to take place in order to convert the hæmatoxylin into hæmatin. The chipped wood is moistened with water, and exposed to the air, frequent stirring over being necessary in order to expose fresh wood to the oxidising influence of the air. In some cases chemicals are added to induce more rapid oxidation, and for this purpose permanganate, sodium nitrite, potassium ferrocyanide are used, either alone or in conjunction with an alkali such as lime, soda or sodium peroxide, which latter acts also as an oxidising agent.

To what extent oxidation is carried out is a matter which depends to a large extent on the method by which the oxidised wood is to be extracted. Where open extraction is used, forced oxidation need not be so drastic as in cases when extraction is done under pressure. Vie (*loc. cit.*) says that the use of autoclaves is coming more into use, so that it is to be presumed that the use of oxidising agents will become more common.

The amount of oxidising agent is, comparatively speaking, small, as if an excess is used the process will be carried too far, with a destruction of dyestuff. This, of course, has to be avoided. From the table of figures given by Vie it would appear that sodium nitrite is the favourite oxidising agent used to the extent of something between 0.5-1 per cent. on the weight of wood used. Noyer suggests ½ lb. per cwt., which is just under 0.5 per cent.

The extraction of the wood is carried out much on the same lines as for tanning materials, and for concentration much the same plant is used.

The yield of extract will vary to some extent, as

the figures given by Vie are of interest in this direction :—

	Method.	25° Baumé Extract.	Dry Extract.	Oxygen Agent.
		Per Cent.	Per Cent.	
Logwood roots -	Open vat	34.5	14.0	Nitrite
Jamaica wood -	Autoclave	30.0	10.0	"
" " -	...	25.8	9.0	Lime
Cape " -	...	30.0	11.0	Nitrite
Mexican " -	Open vat	29.7	13.0	...
Hayti " -	...	27.4	...	...
" " -	...	...	13.0	Nitrite

SECTION IV

METHODS OF EXAMINING TANNING MATERIALS

SECTION IV

METHODS OF EXAMINING TANNING MATERIALS

OFFICIAL METHOD (I.A.L.T.C.)

THE official method of analysing tanning materials as formulated by the International Association of Leather Trade Chemists, and which is official for the Society of Leather Trade Chemists.

Paragraph 1.—The solution for analysis must contain between 3.5 and 4.5 gm. of tanning matter per litre, and solid materials must be extracted so that the greater part of the tannin is removed at a temperature not exceeding 50° C., but if the Teas extractor be used, the first portion of the extract shall be removed from the influence of heat as soon as possible.

Paragraph 2.—The total solubles must be determined by the evaporation of a measured quantity of the solution previously filtered till optically clear, both by reflected and transmitted light; that is, a bright object such as an electric light filament must be distinctly visible through at least 5 cm. thickness, and a layer of 1 cm. deep in a beaker placed in a good light on a black glass or black glazed paper must appear dark and free from opalescence when viewed from above. Any necessary mode of filtration may be employed, but if such filtration causes any appreciable loss when applied to a clear solution, a correction must be determined and applied as described in paragraph 6. Filtration shall take place between the temperatures of 15° C. and 20° C. Evaporation to dryness shall take place between 98.5° C. and 100° C., in shallow, flat-bottomed basins, which shall afterwards be dried until constant at the same temperature, and cooled before weighing for not less than twenty minutes in air-tight desiccators over dry calcium chloride.

Paragraph 3.—The total solids must be determined by drying a weighed portion of the material, or a measured portion of its uniform turbid solution, at a temperature between 98.5° C. and 100° C., in shallow, flat-bottomed basins, which shall afterwards be dried until constant at the same temperature, and cooled before weighing for not less than twenty minutes in air-tight desiccators over dry calcium chloride. "Moisture" is the difference between 100 and the percentage of total solids, and "insoluble" the difference between "total solids" and "total solubles."

Paragraph 4. — *Non-tannins.* — The solution must be detannised by shaking with chromed hide powder till no turbidity or opalescence can be produced in the clear solution by salted gelatine. The chromed powder must be added in one quantity equal to 6.0-6.5 gm. of dry hide per 100 c.c. of the tanning solution, and must contain not less than 0.2 per cent. and not more than 1 per cent. of chromium reckoned on the dry weight, and must be so washed that in a blank experiment with distilled water, not more than 5 mgm. of solid residue shall be left on evaporation of 100 c.c. All water contained in the powder should be determined and allowed for as water of dilution.

The following sections give the detailed method of carrying out the analysis adopted by the S.L.T.C. for the use of its own members.

Paragraph 5.—*Preparation of Infusion.*—Such a quantity of material shall be employed as to give a solution containing as nearly as possible 4 gm. of tanning matter per litre, and not less than 3.5 or more than 4.5 gm. Liquid extracts shall be weighed in a basin or beaker and washed with boiling distilled water into a litre flask, filled up to the mark with boiling water, and well mixed and rapidly cooled to a temperature of 17.5° C., after which it shall be accurately made up to the mark, again well mixed, and filtration at once proceeded with. Sumach and myrobalam extracts should be dissolved at a lower temperature.

Solid extracts shall be dissolved by stirring in a beaker with successive quantities of boiling water, the dissolved portions being poured into a litre flask, and the undissolved being allowed to settle and treated with further portions of boiling water. After the whole of the soluble matter is dissolved, the solution is treated similarly to that of a liquid extract.

Solid tanning materials, previously ground till they will

pass through a sieve of five wires per centimetre, are extracted in Koch's or Procter's extractor with 500 c.c. of water at a temperature not exceeding 50° C., and the extraction continued with boiling water till the filtrate amounts to 1 litre. It is desirable to allow the material to soak for some hours before commencing the percolation, which should occupy not less than three hours, so as to extract the maximum of tannin. Any remaining solubles in the material must be neglected, or reported separately as "difficultly soluble" substances. The volume of liquid in the flask must, after cooling, be accurately made up to 1 litre.

Paragraph 6.—*Filtration.*—The infusion shall be filtered till optically clear (see Par. 2). No correction for absorption is needed for the Berkefeld candle, or for S. and S. 590 paper if a sufficient quantity (250-300 c.c.) is rejected before measuring the quantity for evaporation, and the solution may be passed through repeatedly to obtain a clear filtrate. If other methods of filtration are employed the average correction necessary must be determined in the following manner:—

About 500 c.c. of the same or a similar tanning solution is filtered perfectly clear, and after thorough mixing 50 c.c. is evaporated to determine "total soluble No. 1." A further portion is now filtered in the exact method for which the correction is required (time of contact and volume rejected being kept as constant as possible) and 50 c.c. is evaporated to determine "total soluble No. 2." The difference between No. 1 and No. 2 is the correction sought, which must be added to the weight of the total solubles found in analysis. An alternative method of determining correction, which is equally accurate and often more convenient, is to filter a portion of the tanning solution through the Berkefeld candle till optically clear, which can generally be accomplished by rejecting 300 or 400 c.c., and returning the remaining filtrate repeatedly; and at the same time to evaporate 50 c.c. of the clear filtrate obtained by the method for which correction is required, when the difference between the residues will be the correction sought.

Note.—It is obvious that an average correction must be obtained from at least five determinations. It will be found that this is approximately constant for all materials, and amounts in the case of S. and S. 605, 150 c.c. being rejected, to about 5 mgm. per 50 c.c., and where 2 gm. of kaolin are employed in addition, to 7½ mgm. The kaolin must be previously washed with 75 c.c. of the same liquor, which is

allowed to stand fifteen minutes and then poured off. Paper 605 has a special absorption for a yellow colouring matter often contained in sulphited extracts.

Paragraph 7.—Hide powder shall be of a woolly texture, thoroughly delimed, preferably with hydrochloric acid, shall not require more than 5 c.c. or less than 2.5 c.c. of decinormal NaOH or KOH to produce a permanent pink colour with phenolphthalein on $6\frac{1}{2}$ gm. of the dry powder suspended in water. If the acidity does not fall within these limits it must be corrected by soaking the powder before chroming for twenty minutes in ten to twelve times its weight of water, to which the requisite calculated quantity of standard alkali or acid has been added. The hide powder must not swell in chroming to such an extent as to render difficult the necessary squeezing to 70-75 per cent. of water, and must be sufficiently free from soluble organic matter to render it possible in the ordinary washing to reduce the total solubles in a blank experiment with distilled water below 5 mgm. per 100 c.c. The powder when sent out from the maker shall not contain more than 12 per cent. of moisture, and shall be sent out in air-tight tins.

The detannisation shall be carried out in the following manner: The moisture in the air-dried powder is determined, and the quantity equal to 6.5 gm. actual dry powder is calculated, which will be practically constant if the powder be kept in an air-tight vessel. Any multiple of this quantity is taken according to the number of analyses to be made, and wet back with approximately ten times its weight of distilled water (very woolly powders require slightly more than ten times their weight of water. A powder may be considered "woolly" if it cannot be poured like sand from a beaker). Two gm. per 100 of dry powder of crystallised chromic chloride, $CrCl_3 6H_2O$, is now dissolved in water and made basic with 0.6 gm. of Na_2CO_3 by the gradual addition of 11.25 c.c. of normal Na_2CO_3, thus making the salt correspond to the formula $Cr_2Cl_3(OH)_3$. This solution is added to the powder, and the whole churned for one hour. In laboratories where analyses are continually being made, it is more convenient to employ a 10 per cent. stock solution, made by dissolving 100 gm. of $CrCl_3 6H_2O$ in a little distilled water in a litre flask and very slowly adding a solution containing 30 gm. of anhydrous sodium carbonate, with constant stirring, finally making up to the mark with distilled water and well mixing. Of this solution 20 c.c. per 100 gm. or 1.3 c.c. per 6.5 gm. of dry powder should be used.

At the end of one hour the powder is squeezed in linen to free it as far as possible from the residual liquor, and washed and squeezed repeatedly with distilled water, until, on adding to 50 c.c. of the filtrate 1 drop of 10 per cent. K_2CrO_4 and 4 drops of decinormal silver nitrate, a brick red colour appears. Four or five squeezings are usually sufficient. Such a filtrate cannot contain more than 0.001 gm. of NaCl in 50 c.c.

The powder is then squeezed to contain 70-75 per cent. of water, and the whole weighed. The quantity Q containing 6.5 gm. dry hide is thus found, weighed out, and added immediately to 100 c.c. of the unfiltered tannin infusion along with $(26.5 - Q)$ of distilled water. The whole is corked up and agitated for fifteen minutes in a rotating bottle at not less than 60 revs. per minute. It is then squeezed immediately through linen, 1 gm. of kaolin added to the filtrate, stirred and filtered through a folded filter of sufficient size to hold the entire filtrate, returning till clear, and 60 c.c. of the filtrate is evaporated and reckoned as 50 c.c., or the residue of 50 c.c. is multiplied by 6/5. The non-tannin filtrate must give no turbidity with a drop of 1 per cent. gelatine, 10 per cent. salt solution. The kaolin may be used by mixing it with the hide powder in the shaking bottle.

Paragraph 8.—The analysis of used liquors and spent tans shall be made by the same methods as are employed for fresh tanning materials. The liquors or infusions being diluted, are concentrated by boiling *in vacuo*, or in a vessel so closed as to restrict access of air, until the tanning matter is if possible between 3.5 and 4.5 gm. per litre, but in no case beyond a concentration of 10 gm. per litre of total solids, and the weight of hide powder used shall not be varied from 6.5 gm.

The results shall be reported as shown by the direct estimation, but it is desirable that in addition efforts shall be made, by determination of acids in the original solution and in the non-tannin residue, to ascertain the amount of lactic and other non-volatile acids absorbed by the hide powder, and hence returned as "tanning matters." In the case of tans it must be clearly stated in the report whether the calculation is on the sample with moisture as received, or upon some arbitrarily assumed percentage of water; and in that of liquors whether the percentage given refers to weight or to grams per 100 c.c., and in both cases the specific gravity shall be reported.

Paragraph 9.—All evaporation shall be rapidly conducted at steam temperature in shallow flat-bottomed basins of not

less than 5.5 cm. diameter to apparent dryness; and shall be subsequently dried between 98°-100° C. in a water or steam oven until of constant weight, and shall be afterwards cooled in small air-tight desiccators over dry calcium chloride for at least twenty minutes, and then weighed rapidly. Not more than two basins shall be placed in one desiccator, and the basins must not be wiped after removal from the desiccator. All analyses reported must be the average result of duplicate determinations which must agree in the case of liquid extracts within 0.6 per cent., and of solid extracts within 1.5 per cent., or the analysis shall be repeated until such agreement is obtained.

N.B.—Further details regarding manipulation and calculation of results, etc., can be found in "Practical Leather Chemistry," by the present author.

AMERICAN METHOD (A.L.C.A.)

The official method of analysing tanning materials as formulated by the American Leather Chemists' Association, and published by them both in the *Journal* and in the form of a special leaflet, is as follows:—

I. Raw and Spent Materials.

(1) Caution.

Proper care must be taken to prevent any change in the water content of raw materials during the sampling and preliminary operations.

(2) Preparation of Sample.

The sample must be ground to such a degree of fineness that the entire sample will pass through a sieve of 20 meshes to the inch (linear).

(*a*) The temperature used for drying samples of spent material for grinding must not exceed 60° C.

(*b*) Samples of raw material too wet to be ground may be dried before grinding as in (*a*). In this case a preliminary water determination must be made according to (IV.) on the sample as received. If the portion of the sample taken for the water determination is in pieces too large to dry properly, it is permissible to reduce these to smaller size as rapidly and with as little loss of water as possible.

(3) WATER DETERMINATION.

Ten gm. of the ground material shall be dried in the manner and for the period specified for evaporation and drying in extract analysis (see IV.).

(4) AMOUNT OF SAMPLE TO BE EXTRACTED.

Such an amount of raw material shall be extracted as will give a solution containing as nearly as practicable 0.4 gm. tannin to 100 c.c. (not less than 0.375 or more than 0.425). Of spent materials such an amount shall be taken as will give a solution of as nearly as practicable the above concentration.

(5) EXTRACTION.

Extraction shall be conducted in an apparatus consisting of a vessel in which water may be boiled, and a container for the material to be extracted. The container shall be provided above with a condensation chamber so arranged that the water formed from the condensed steam will drip on the material to be extracted, and provided below with an arrangement of outlets such that the percolate may either be removed from the apparatus or be delivered to the boiling vessel. The boiling vessel must be so connected that it will deliver steam to the condensation chamber, and that it may receive the percolate from the container. The condensation water from the condenser must be at approximately the boiling temperature when it comes in contact with the material to be extracted.

The material of which the boiling flask is composed must be inert to the extractive solution. Suitable provision must be made for preventing any of the solid particles of the material from passing into the percolate.

(A) *Woods, Barks, and Spent Materials.*—500 c.c. of the percolate shall be collected outside in approximately two hours, and the extraction continued with 500 c.c. for fourteen hours longer by the process of continuous extraction with reflux condenser. The applied heat shall be such as to give condensation approximately 500 c.c. in one and a half hours.

(B) *Materials Other than Woods, Bark, and Spent.*—Digest the material in the extractor for one hour with water.

at room temperature, and then extract by collecting 2 litre of percolate outside in approximately seven hours.

(6) Analysis.

The percolate shall be heated at 80° C., be cooled, made to the mark and analysed according to the official method of extracts.

II. Analysis of Extract.

(7) Amount and Dilution for Analysis.

(A) *Fluid Extracts.*—Fluid extracts shall be allowed to come to room temperature, be thoroughly mixed, and such quantity weighed for analysis as will give a solution containing as nearly as possible 0.4 gm. tannin to 100 c.c. (not less than 0.375 nor more than 0.425). Precautions must be taken to prevent loss of moisture during weighing. Dissolve the extract by washing it into a litre flask with 900 c.c. of distilled water at 85° C.

Cooling.—(*a*) The solutions prepared as above shall be cooled rapidly to 20° C. with water at a temperature of not less than 19° C., be made to the mark with water at 20° C., and the analysis proceeded with at once; or

(*b*) The solution shall be allowed to stand over night, the temperature of the solution not being permitted to go below 20° C., be brought to 20° C. with water at not less than 19° C., be made to the mark with water at 20° C., and the analysis proceeded with.

(B) *Solid and Powdered Extracts.*—Such an amount of solid or powdered extract as will give a solution of the strength called for under liquid extracts shall be weighed in a beaker with proper precautions to prevent change of moisture. One hundred c.c. of distilled water at 85° C. shall be added to the extract and the mixture placed on the water-bath, heated and stirred, until a homogeneous solution is obtained. When dissolved, the solution shall immediately be washed into a litre flask with 800 c.c. of distilled water at 85° C., be cooled, etc., as under (*a*) above.

Note.—It is permissible to make up 2-litre instead of 1-litre solutions, dissolving by washing into flask with 1,800 c.c. water at 85° C. in case of fluid extracts and 1,700 c.c. water at 85° C. in case of solid or powdered extracts.

(8) TOTAL SOLIDS.

Thoroughly mix the solutions; pipette 100 c.c. into tared dish, evaporate and dry as directed under "Evaporation and Drying" (see IV.).

(9) WATER.

The water content is shown by the difference between 100 per cent. and the total solids.

(10) SOLUBLE SOLIDS.

S. and S. No. 590, or Munktell's No. 1F, 15 cm. single, pleated, filter paper shall be used for the filtration.

The kaolin used shall answer the following test: 2 gm. kaolin digested with 200 c.c. of distilled water at 20° C. for one hour shall not give more than 1 mg. of soluble solids per 100 c.c., and shall be neutral to phenolphthalein. To 1 gm. kaolin in a beaker add sufficient solution to fill the paper, stir, and pour on paper. Return filtrate to paper when approximately 25 c.c. has collected, repeating operation for one hour, being careful to transfer all kaolin to the paper. At the end of the hour remove solution from filter paper, disturbing the kaolin as little as possible. Bring so much as needed of the original solution to exactly 20° C. as described under (7), refill the paper with this solution and begin to collect the filtrate for evaporating and drying so soon as it comes *clear*. The paper must be kept full and the temperature of the solution on the filter must not fall below 20° C. nor rise above 25° C. during this part of the filtration. The temperature of the solution used for refilling the paper must be kept uniformly at 20° C. and the funnels and receiving vessels must be kept covered.

Pipette 100 c.c. of clear filtrate into tared dish; evaporate and dry as under (8).

(11) INSOLUBLES.

The insoluble content is shown by the difference between the total solids and the soluble solids, and represents the matters insoluble in a solution of the concentration used under the temperature conditions prescribed.

(12) NON-TANNINS.

The hide powder used for the non-tannin determination shall be of woolly texture well delimed, and shall require

between 12 and 13 c.c. of N/10 NaOH to neutralise 10 gm. of the absolutely dry powder.

(*a*) Digest the hide powder with ten times its weight of distilled water till thoroughly soaked. Add 3 per cent. of chrome alum, $Cr_2(SO_4)_3K_2SO_4 24H_2O$, in 3 per cent. solution calculated on the weight of the air-dry powder. Agitate frequently for several hours and let stand over night. Squeeze and wash by digesting with four successive portions of distilled water, each portion equal in amount to fifteen times the weight of the air-dry powder taken. Each digestion shall last for fifteen minutes, and the hide powder shall be squeezed to approximately 75 per cent. water after each digestion except the last, a press being used if necessary. The wet hide powder used for the analysis shall contain as nearly as possible 73 per cent. of water, not less than 71 per cent. nor more than 74 per cent. Determine the moisture in the wet hide powder by drying approximately 20 gm. (see IV.). To such quantity of the wet hide as represents as closely as practicable 12½ gm. (not less than 12.2 nor more than 12.8) of absolutely dry hide add 200 c.c. of the original analysis solution and shake immediately for ten minutes in some form of mechanical shaker. Squeeze immediately through linen, add 2 gm. of kaolin (answering test described under (9)) to the detannised solution and filter through single folded filter (No. 1F Swedish recommended) of size sufficient to hold the entire filtrate, returning until clear. Pipette 100 c.c. of filtrate into tared dish, evaporate and dry as in (8).

The weight of the non-tannin residue must be corrected for the dilution caused by the water contained in the wet hide powder.

Funnels and receiving vessels must be kept covered during filtration. Flasks graduated to deliver 200 c.c. are recommended for measuring the analysis solution to be detannised.

(*b*) Digest the hide powder with the amount of water and add the amount of chrome alum in solution directed under (*a*).

Agitate in some form of mechanical shaker for one hour and proceed immediately with washing and subsequent operations as directed under (*a*).

Note.—In order to limit the amount of dried hide powder used, determine the moisture in the air-dry powder and calculate the quantity equal to 12½ gm. of actual dry hide powder. Take any multiple of this quantity according to the number of analyses to be made, and after chroming and

washing as directed, squeeze to a weight representing as nearly as possible 73 per cent. of water. Weigh the whole amount and divide by the multiple of the $12\frac{1}{2}$ gm. of actual dry hide powder taken to obtain the weight of wet hide powder for 200 c.c. of solution.

(13) TANNIN.

The tannin content is shown by the difference between the soluble solids and the corrected non-tannins, and represents the matters absorbable by hide under the conditions of the prescribed methods.

III. Analysis of Liquor.

(14) DILUTION.

Liquors shall be diluted for analysis with water at room temperature so as to give as nearly as possible 0.7 gm. solids per 100 c.c. of solution. Should a liquor be of such character as not to give a proper solution with water of room temperature, it is permissible to dilute with water at 80° C. and cool rapidly.

(15) TOTAL SOLIDS.

To be determined as in extract analysis.

(16) SOLUBLE SOLIDS.

To be determined as in extract analysis.

(17) INSOLUBLES.

Determined as in extract analysis.

(18) NON-TANNINS.

To be determined by shaking 200 c.c. of solution with an amount of wet chromed hide powder, containing as nearly as possible 73 per cent. water, corresponding to an amount of dry hide powder shown in the following table:—

Tannin Range per 100 c.c.	Dry Powder per 200 c.c.
0.35 to 0.45 gm.	9.0 to 11.0 gm.
0.25 to 0.35 „	6.5 to 9.0 „
0.15 to 0.25 „	4.0 to 6.5 „
0.00 to 0.15 „	0.0 to 4.0 „

Solutions to be shaken for non-tannins as in extract analysis, and 100 c.c. evaporated as in extract analysis.

IV. Temperature, Evaporation and Drying, Dishes.

(19) TEMPERATURE.

The temperature of the several portions of each solution pipetted for evaporating and drying, that is, the total solids, soluble solids, and non-tannins, must be identical at the time of pipetting.

(20) EVAPORATION.

All evaporations and dryings shall be conducted in the form of apparatus known as the "Combined Evaporator and Dryer," at a temperature not less than 98° C. The time for evaporation and drying shall be sixteen hours.

(21) DISHES.

The dishes used for evaporation and drying of all residues shall be flat-bottomed glass dishes of not less than $2\frac{3}{4}$ in. diameter nor more than 3 in. in diameter.

SECTION III

MANUFACTURE OF TANNING EXTRACTS

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MANUFACTURE OF TANNING EXTRACTS

ONE of the first points for consideration in the manufacture of extracts is the nature of the water supply, for, as might be appreciated, all other things being equal, the quality of the extract will depend largely on the water used. The mineral salts present in water vary with the source of supply, but speaking generally the following may or may not be present:—

(1) Bicarbonates of calcium and magnesium, together known as temporary hardness.
(2) Sulphates of lime and magnesium, known as permanent hardness.
(3) Chlorides of magnesium, potassium, and sodium (more usually the latter).
(4) Sodium carbonate.
(5) Iron.

It has been shown by Nihoul and his co-workers that all soluble salts cause a more or less loss in the yield of tannin either by precipitation or oxidation (*Collegium*, 1903; "Bulletin," Soc. Belg. Chem., 1903; *J.S.C.I.*, 1902). Sodium carbonate if present to the extent of more than a trace will cause darkening, while, if iron is present, an objectionable blue-black colour will be formed. The present writer found that a water containing 0.15 part per 100,000 of Fe gave a *deep* blue colour when treated with tannin solution and allowed to stand for a short time. The methods used in testing a water will be found in the author's "Practical Leather Chemistry" (Crosby Lockwood).

For the guidance of others the author reproduces five analyses of various Belgian waters by Nihoul, with which experimental work was done (Abstr., *J.S.C.I.*, 1902).

PARTS PER 100,000.

	1. Distilled.	2. Somewhat Hard.	3. Rich in Sulphates.	4. Rich in Chlorides.	5.[1] Hard.	6.[1] Very Hard.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Total hardness	...	19.50	39.00	41.24	46.88	78.00
Temporary hardness	...	9.92	23.34	22.90	21.68	50.54
Permanent hardness	...	9.58	15.66	18.34	25.20	27.46
Sulphur trioxide	...	3.09	10.56	4.45	27.00	33.83
Chlorine	...	4.76	0.67	14.28	39.55	46.55
Equivalent to salt	...	7.84	1.10	23.53	65.17	76.71
Lime, CaO	.	10.67	20.50	11.20	27.64	45.89
Magnesia, MgO	...	0.50	0.16	0.08	1.58	0.16

Extracting tanning materials in the cold, water 3 darkened the colour of pine extract and gave a dull colour with sumach, both these defects being still more marked when water 4 was used for extracting. Unusual turbidness was formed with sumach when extracted with waters 5 and 6, and in addition gave dark coloured liquors. In hot extraction it was found that the hardness caused considerable loss of tannin, and chlorides affect the tannin in oak, sumach and pine but not that present in valonia.

Water for extraction purposes may be softened by any of the appropriate methods. The question of softening is one which demands expert attention, as in a few cases it is found that the expenditure involved in treatment is unwarranted owing to the nature of the supply. Such a remark applies to comparatively soft water.

The removal of temporary hardness is a simple matter, this being done by means of lime (Clark's process):—

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O$$
$$Mg(HCO_3)_2 + 2Ca(OH)_2 = Mg(OH)_2 + 2CaCO_3 + H_2O.$$

It will be seen that the temporary hardness is completely removed, leaving nothing in solution as the result of the reaction. This is not the case with the permanent hardness, where magnesium and calcium sulphates are replaced by sodium sulphate. This, however, is a distinct advantage, as magnesium sulphate and calcium sulphate give insoluble

[1] Fair amount of iron also present.

precipitates with tannin, which in extraction means a loss. Hence, if these are removed such loss does not take place, as no precipitation occurs with sodium sulphate. Complete softening is done by lime and soda under conditions which vary somewhat with the type of water being dealt with, and fuller information can be found in the larger manuals on water supply.

A word might be added in passing on the "Permutit" method of water softening. In this process the water to be softened is passed through a layer of an artificial zeolite (a silicate of alumina and soda), when an interchange of bases takes place, thus:—

$$\text{Sodium permutit} + Ca(HCO_3)_2 = \text{Calcium permutit} + 2NaHCO_3.$$
$$\text{Sodium permutit} + MgSO_4 = \text{Magnesium permutit} + Na_2SO_4.$$

Hence with one clean sweep all calcium and magnesium is removed from the water. The only point to guard against is the bicarbonate formed in replacing the temporary hardness. This should be treated with an acid so as to make quite neutral, and under working conditions would not prove a difficult matter. On the whole it is a process which on account of simplicity should appeal to manufacturers. Further, the Permutit can be regenerated by washing with a salt solution, when the process reverse to softening takes place.

$$\text{Calcium permutit} + NaCl = \text{Sodium permutit} + \text{Calcium chloride}.$$

It follows from the remarks which have been made that for extraction purposes the purer the water the better. The influence on the soluble salts in extraction is shown by the table on page 106 by Nihoul who used the waters previously mentioned to extract four materials.

Another point for attention is the temperature at which tanning materials should be extracted without any undue loss due to decomposition. This question has been thoroughly investigated by Parker and Procter (*J.S.C.I.*, 1895, p. 635) and discussed by Blockey (*Leather World*, 1911, p. 116). The former chemists extracted various materials at different temperatures and determined the tannin so extracted. Taking the maximum extracted as 100, the table on page 107 gives the percentage of the total tannin extracted at the various temperatures.

Water.	Tanning Material.															
	Oak Bark.								Pine Bark.							
	Hot Extraction.				Cold Extraction.				Hot Extraction.				Cold Extraction.			
	Tannin.	Non-Tans.	Loss in Tannin.	Mineral Weighting.	Tannin.	Non-Tans.	Loss in Tannin.	Mineral Weighting.	Tannin.	Non-Tans.	Loss in Tannin.	Mineral Weighting.	Tannin.	Non-Tans.	Loss in Tannin.	Mineral Weighting.
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
I. Distilled water	14.2	4.4	*Nil*	0.2	9.9	3.1	*Nil*	0.0	22.4	3.1	*Nil*	0.2	18.0	1.6	*Nil*	0.0
II. Somewhat hard	13.1	5.6	9.2	0.4	9.3	3.5	0.5	0.1	22.3	3.7	0.4	-0.1	17.4	3.1	3.2	0.2
III. Rich in sulphates	11.8	6.7	17.6	0.4	8.4	3.9	15.2	0.4	20.5	4.3	8.4	-0.1	18.2	2.8	+	0.1
IV. Rich in chlorides	10.3	6.5	28.6	0.2	8.8	3.9	11.2	0.0	19.6	5.3	12.4	0.6	17.7	3.1	1.4	-0.0
V. Hard	...	...	...	..	...	...	...	...				...	..	...	...	...
VI. Very hard	6.9	6.3	51.9	0.1	8.2	4.9	17.5	0.1	17.6	6.7	21.5	0.1	16.4	4.3	9.1	0.2

Water.	Tanning Material.															
	Sumach.								Valonia.							
	Hot Extraction.				Cold Extraction.				Hot Extraction.				Cold Extraction.			
	Tannin.	Non-Tans.	Loss in Tannin.	Mineral Weighting.	Tannin.	Non-Tans.	Loss in Tannin.	Mineral Weighting.	Tannin.	Non-Tans.	Loss in Tannin.	Mineral Weighting.	Tannin.	Non-Tans.	Loss in Tannin.	Mineral Weighting.
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
I. Distilled water	23.0	10.9	*Nil*	0.0	17.9	11.1	*Nil*	0.0	35.8	10.8	*Nil*	0.0	33.1	8.4	*Nil*	0.0
II. Somewhat hard	19.6	15.7	15.1	0.1	14.3	11.2	20.2	0.2	33.9	12.3	5.4	0.5	28.0	8.7	15.5	0.2
III. Rich in sulphates	12.1	18.0	47.6	0.1	12.6	10.9	29.4	0.5	33.2	14.5	7.3	1.0	30.1	10.3	9.02	0.3
IV. Rich in chlorides	7.0	24.5	69.2	0.4	13.4	12.8	25.2	0.6	33.3	11.9	7.1	0.8	30.5	11.1	8.1	1.0
V. Hard	2.1	16.3	90.8	0.0	10.7	13.2	40.2	0.3	29.1	12.8	18.7	0.6	27.0	10.1	18.5	0.5
VI. Very hard	...	...	...	...	...	...	...	...	...	...	...	...	...		...	...

Temperature of extraction, °C.		15	15-30	30-40	40-50	50-60	60-70	70-80	80-90	90-100	Boiled for ½ hr.
Oak bark	A. Per cent. of tannin on the maximum	61.9	70.7	83.5	84.2	87.6	95.5	95.7	100.0	100.0	93.7
	B. Per cent. of colour on the maximum	57.4	64.5	76.1	80.0	84.0	92.7	98.7	93.2	94.6	100.0
Myrobalams	A. Per cent. of tannin on the maximum	79.2	83.6	89.8	93.0	96.4	96.6	96.8	97.4	100.0	98.1
	B. Per cent. of colour on the maximum	97.4	82.5	82.7	84.4	87.6	89.3	94.1	96.7	91.0	100.0
Valonia	A. Per cent. of tannin on the maximum	70.5	74.5	86.2	86.2	100.0	99.0	99.5	95.0	94.0	90.6
	B. Per cent. of colour on the maximum	74.6	78.0	76.2	74.6	76.2	84.7	84.7	84.7	90.6	100.0
Mimosa	A. Per cent. of tannin on the maximum	66.2	90.2	94.0	94.4	95.0	98.4	100.0	96.2	94.0	91.8
	B. Per cent. of colour on the maximum	51.1	54.2	56.5	61.8	79.9	81.6	85.5	93.8	100.0	98.4
Sumach	A. Per cent. of tannin on the maximum	70.0	86.7	91.1	99.0	100.0	93.6	89.1	83.2	81.7	74.8
	B. Per cent. of colour on the maximum	63.6	57.0	57.8	52.9	56.5	66.6	72.8	82.7	87.7	100.0
Quebracho	A. Per cent. of tannin on the maximum	35.0	46.5	54.4	69.5	76.0	80.0	88.0	100.0	89.8	...
	B. Per cent. of colour on the maximum	71.3	68.7	65.2	60.0	60.4	59.9	67.4	74.3	100.0	...
Mangrove	A. Per cent. of tannin on the maximum	61.6	76.3	82.4	87.7	96.2	94.7	96.7	100.0	95.7	...
	B. Per cent. of colour on the maximum	64.7	70.0	71.7	73.8	72.8	90.0	82.8	77.8	100.0	...
Gambier block	A. Per cent. of tannin on the maximum	50.1	69.6	81.6	89.6	93.6	94.6	94.7	95.2	96.4	100.0
	B. Per cent. of colour on the maximum	33.5	34.0	55.0	61.0	62.5	66.0	63.5	74.0	83.0	100.0

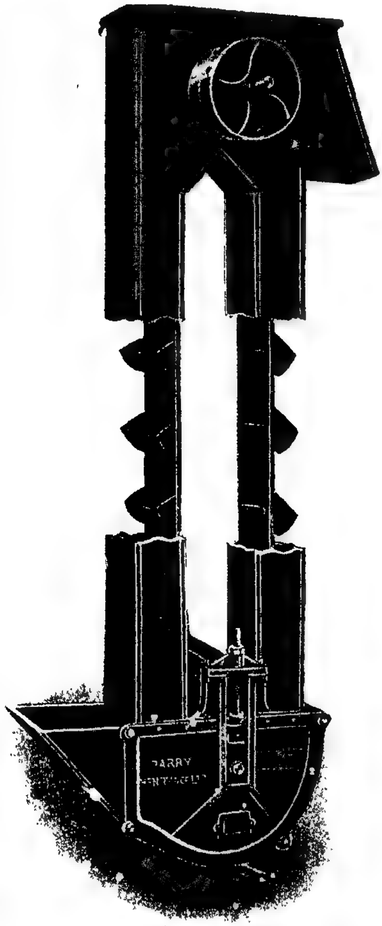

FIG. 6.—Elevator.

These figures clearly indicate that there is a maximum temperature of extraction for each material, thus:—

Oak bark	80°-90° C.	Sumach	50°-60° C.
Myrobalams	90°-100° C.	Quebracho	80°-90° C.
Valonia	50°-60° C.	Mangrove	80°-90° C.
Mimosa	70°-80° C.	Block gambier	100° C.

It is to be noticed, too, that prolonged heating at 100° C. leads to an increase in colour, an important matter to the extract maker who aims at as light a material as is possible under working conditions.

These figures, of course, apply to open extraction and not to pressure treatment in autoclaves where conditions are quite different.

Handling of Materials.

Owing to increasing costs of hand labour in all parts of the world, it is found to be necessary, where at all possible, to adopt some form of mechanical handling of material. Local conditions have an important bearing as to the exact form of mechanical handling that should be adopted, and it is generally necessary to consider each case by itself. Fig. 6 represents a type of elevator that is well adapted for raising crushed material in an extract factory. The type shown is constructed in canvas belting with gun-metal buckets, so that there can be no contact of iron or steel with the raw material. The capacities of this class of elevator would vary with the weight per cubic foot of the raw material and the condition of grinding, but it may be approximated that with buckets of 8 in. width about 3 tons per hour of crushed bark could be dealt with, the elevator running at a speed of about 120 ft. per minute. For conveying material in a horizontal direction, it is customary to use band conveyers, running at a speed of about 300 ft. per minute, and with a 12-in. band the capacity would vary from 10-12 tons of bark per hour. A type of band conveyer is indicated in Fig. 7, but such conveyers can also be arranged with throw-off carriages, so that the material can be delivered at any desired point in the travel of the conveyer.

An alternative form of conveyer for horizontal or medium inclinations or gradients is the Archimedean screw type as indicated in Fig. 8.

This type of conveyer is either of the ribbon type as shown in the illustration, which is generally used for very light

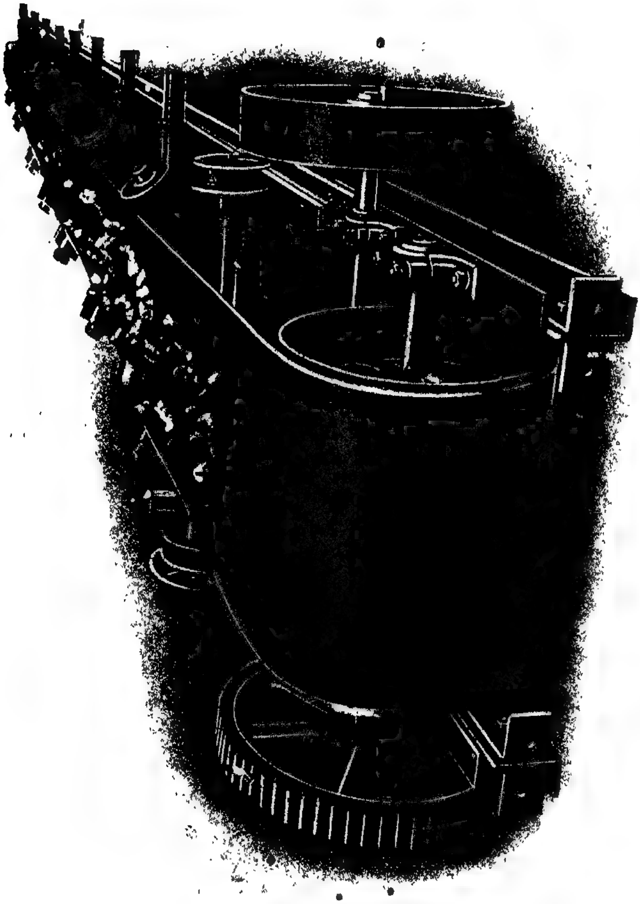

FIG. 8.—Screw Conveyer.

materials, or of the solid Archimedean screw type for material of irregular dimensions. For handling of raw material for extract making it is necessary to have the blades constructed in Muntz metal or brass, and the troughing should be constructed in wood, or if in steel, it should be lined with copper or Muntz metal sheets. To draw off the material at intermediate points of the Archimedean, small doors can be provided with leading-off shoots as required. An approximate capacity for an Archimedean conveyer running at 60 revs. per minute with the screw 10 in. diameter, would be about 4 tons per hour of crushed bark.

Motive Power.—It is difficult to indicate a hard and fast line as to the best form of motive power for an extract factory. A convenient supply of power might be obtained locally from an electric supply station, and it would be found convenient to operate the bulk of the machinery electrically. On the other hand, as the evaporators are usually worked with exhaust steam, and steam boilers have in any case to be installed, it is generally an advantage to have the prime mover steam driven, so that the exhaust steam can be led to the evaporators, care being taken to intercept any oil so that it would not be allowed to enter the calandrias of the evaporators.

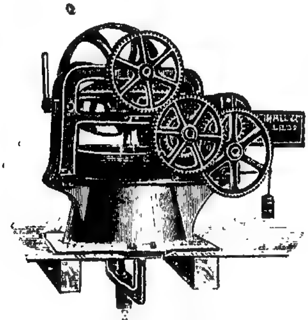

FIG. 9.- Combined Bark Cutter and Mill.

Grinding and Preparation of Raw Material.—One of the first operations in extract manufacture is reducing the raw material to a degree of fineness essential for thorough extraction, and for this purpose, crushers, chippers, etc., are employed according to the nature of the raw material.

The idea of chopping is to open the ends of the material, and the grinding is not grinding in the true sense of pulverising or disintegrating, but of shredding, and thus allowing of a better side penetration. Any crushing action which condenses or squeezes the various fibres or strands together must consequently make penetration more difficult.

Fig. 9 shows a combined cutter and mill for barks, the material first being cut into definite lengths and then ground in the mill below.

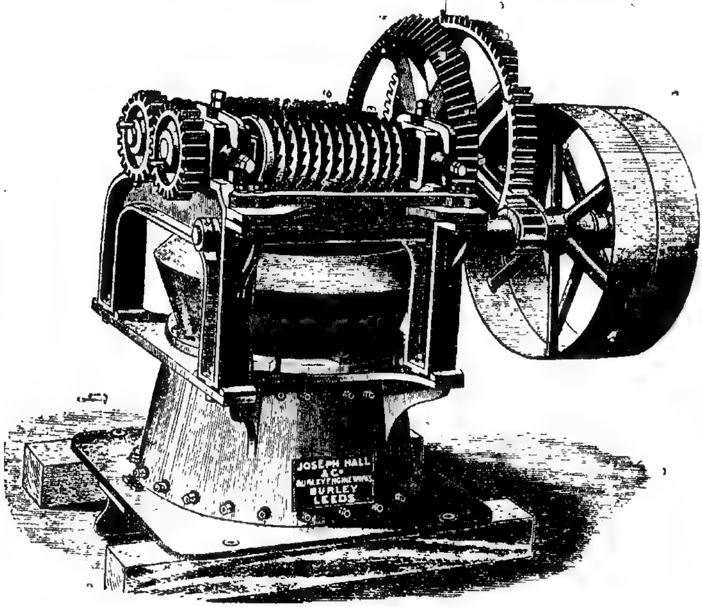

FIG. 10.—Mill.

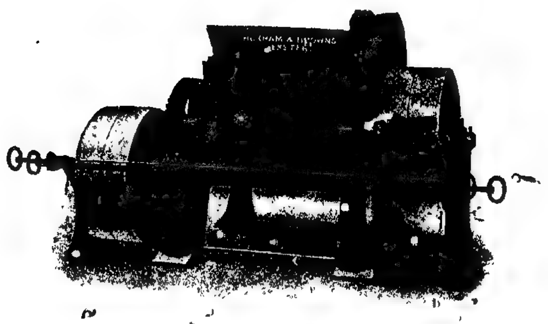

FIG. 11.—Four-Roll Machine.

The capacity of the machine is up to 12 tons per ten-hour day, the amount varying, of course, with the size of the plant.

Another type of machine is shown in Fig. 10, which is fitted with cutters with serrated teeth for breaking, instead of knives for cutting, while a four-roll bark crusher is illus-

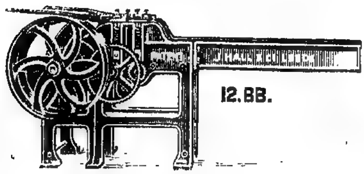

FIG. 12.—Bark Chopper.

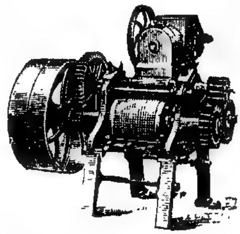

FIG. 13.—Myrobalam Mill (Hall & Co.).

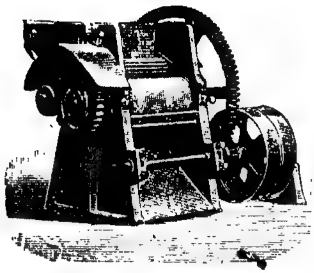

FIG. 14.—Mill (Huxham and Browns).

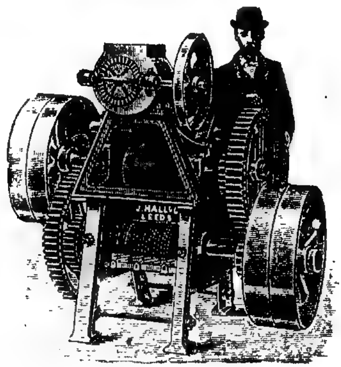

FIG. 15.—Valonia Mill.

trated in Fig. 11. This is specially suited for thick heavy barks, the upper set of teeth being made in cast iron for the preliminary breaking, and the bottom serrated cutters, being of steel of closer gauge, break up the bark to the required degree.

The output of the former type is up to 10 tons per ten-hour day, and requires only one man in attendance. For very hard barks which cannot always be dealt with in the usual type of chopper, that shown in Fig. 12 has

been found very effective. Many barks are merely treated by passing through a bark chopper with quick revolving knives or cutters. The rate of feed can be so adjusted by this method, that the bark can be shaved off in such fine strips, that it would be suitable for extraction without the intervention of other machines.

When dealing with such tanning materials as myrobalams, valonia, special designs of breaking machines are necessary. Three such types are shown in Figs. 13-15.

The question of grinding and adequate preparation of the raw material is one that is best determined as the result of experience. Too fine grinding is not desirable in one sense, as clogging in the leaches may take place, with all its attendant difficulties; on the other hand, the finer the grinding the more thorough can the extraction be made. Therefore, between these two sets of factors, a happy medium must be struck.

The following comparative figures clearly illustrate the advantage of fine grinding, neglecting for the moment the question of clogging.

TANNIN IN SPENT MATERIAL.

	Per Cent.
Chopped unground	8.7
Coarsely ground	8.3
Medium ground	6.8
Finely ground	6.1

Six per cent. of tannin in the spent bark is, of course, on the high side, and a much lower figure should be aimed at. An analysis of a well extracted bark is given below, and indicates the extent to which extraction can be carried:—

	Per Cent.
Tannin	0.94
Non-tannins	0.76
Insolubles	48.30
Moisture	50.00
	100.00

During the process of disintegration, the plant should be so arranged that no dust is lost, as in a number of instances the dust contains a higher proportion of tannin than the residual fibrous matter. Some figures given by Fraymouth and Pilgrim relating to sal bark, clearly illustrate this point.

	Powder.	Fibre.
	Per Cent.	Per Cent.
Tannin	12.33	3.11
Non-tannins	8.42	4.09
Insoluble matter	74.25	92.80
	95.00	100.00

Extraction.—The extraction of the tannin from the ground material may be carried out by a number of processes, thus:—

(1) Open vat extraction.
(2) Rotary system.
(3) Pressure autoclaves.
(4) Oven vat with Archimedean screw.
(5) Vacuum extraction (Nance process).
(6) Roller extraction.
(7) Gas lift agitation method.

Whatever process is employed, it is essential that no iron be used in the filling of the plant owing to discoloration, hence, apparatus is made either of wood with copper or brass fittings and pipework, or in concrete.

Open Vat Extraction.—One of the most satisfactory methods of extraction is by means of the ordinary open vat

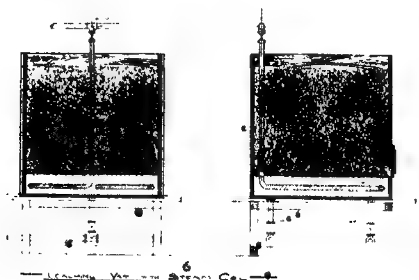

FIG. 16.—Extraction Vat.

worked in a series. A simple vat made of wood and fitted with a perforated false bottom and steam coil for heating is shown in Fig. 16.

For the filling of vats on a large scale, the general practice is to use conveyers which are either of the Archimedean screw type or belt conveyer with a throw-off carriage (see p. 111).

For the emptying of wooden vats it is found more convenient to have suitable doors generally made of gun-metal on the side of the vat, or circular doors at the bottom of the vat permitting the spent tan to drop into small trucks or on to some form of conveyer by which it is taken to the boiler house and dried, etc., by suitable means.

With this vat, water, or liquor from a previous vat, is run in up to a few inches above the false bottom, when the bark is added together with water. Heating is carried out by means of the steam coil which at the same time effects a certain amount of agitation. It must be remembered, however, that the water of condensation produced goes to dilute the liquor, which in turn means extra cost in evaporation. What appears to be a better form of heating is by means of

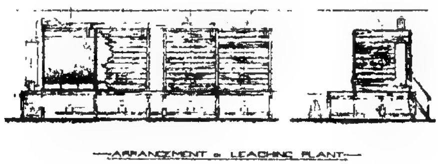

FIG. 17.—Vats with Calorifiers.

a calorifier, which acts as an independent heater. A battery of leaches with this attachment is illustrated in Fig. 17.

In working such a series of vats with an attached calorifier, the valve at the bottom of the leach is opened, which couples up to the connecting pipe of a centrifugal pump, and discharges into the wooden trough arranged above the leaches; then, if it is desired to increase the temperature of the liquor in one particular vat, this is done by circulating the liquor for a given period through the calorifier.

A definite example of the manner in which dilution of liquor occurs through heating by means of direct steam may be stated thus—

A vat containing 10 tons of liquor has to be raised from 20°-90° C. with steam at 30 lbs. pressure. Allowing 10 per cent. for losses, the steam required is roughly 1.35 tons, making the total liquor (original liquor and condensed steam) 10.35 tons, a dilution of 15 per cent. As against the method of running direct steam for heating purposes, it is obvious

that practically the same heating effect is secured by taking advantage of the latent heat of the steam in a calorifier or heater where the liquor to be heated does not come into contact with the condensed steam.

In working a series of vats or leaches, each charge of water works through the whole series, so that at the end of the process one has a fairly concentrated liquor. Incidentally, each vat of bark or other material is leached several times to illustrate the moving of the liquor and the discharging of spent bark. The following example will be given. It will be assumed that a series or battery of eight leaches are in operation, and that vat 4 is the one from which the spent bark is next to be removed and a fresh charge added :—

The strong liquor in 3 is run off to the clarifiers and all remaining liquors moved one up the series.

After vat 4 has been drained, the door is opened and the spent bark removed, and it is then ready to receive a new lot of bark. This, having been put in, the liquor from 3 is pumped into 4 and so on as illustrated below, leaving vat 5 empty of liquor. This latter vat is charged with a fresh lot of water and after extraction constitutes the next vat to be emptied of spent bark.

This vat is now charged with fresh water at 100° C. for extraction. The point to be borne in mind is that the vat containing the bark that is fresh receives the strongest liquor so as to build up its gravity before drawing off.

As the bark proceeds through the series of extractions (in this case 1-8), nearing the point of being almost spent, the temperature of extraction is increased, which in the last extraction when the fresh water is used, is about 100° C. Early extractions are done at a lower temperature, so that, as the somewhat strong liquor passes through fresh bark, clear liquors are formed by the fact that the difficultly soluble material extracted at the higher temperature is gradually precipitated and filtered out in the bark.

A golden rule for open vat extraction is to extract the major part of the tannin at as low a temperature as possible so as to avoid decomposition and darkening in colour of the liquor.

In fixing the number of units to form a system, the minimum should be six, and much labour is saved by using a large number.

The Rotary System.—In this method, a series of drums are used as extraction vessels, and by the continual agitation brought about by rotation, a very thorough extraction takes

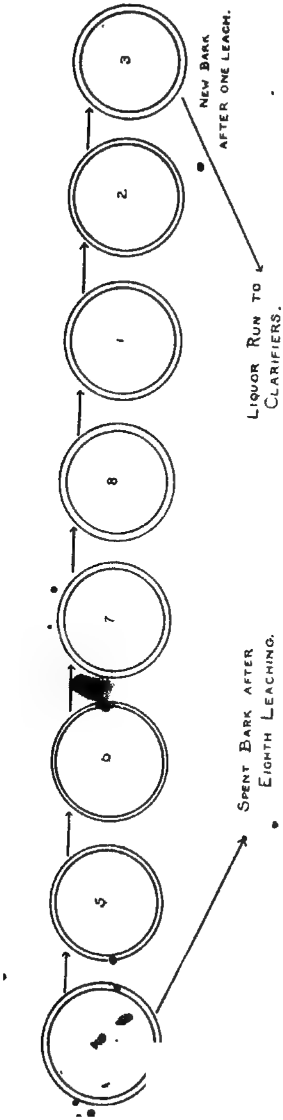
New Bark after one leach.
Liquor Run to Clarifiers.
Spent Bark after Eighth Leaching.
3
2
1
8
7
6
5

FIG. 18.

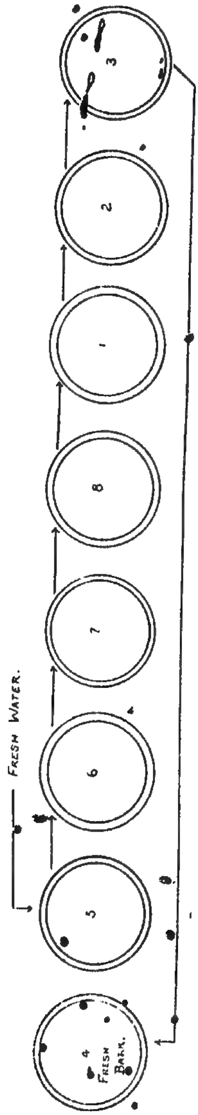
Fresh Water.
4 Fresh Bark.
3
2
1
8
7
6
5

FIG. 19.

place. The series of drums, one of which is shown in Fig. 20, are operated in exactly the same way as a series of vats, *i.e.*, the liquor passing from one drum to the other, the bark remaining in the drum, and receiving further extractions, the number depending on the number of units to the plant. Although not in very large use, this method of extraction is said to give very good results. Guisiana has described (*Le Cuir*) a method of extraction very similar to the rotary leach system of Kestner. A series of five drums are used, each fitted with a steam injector at the

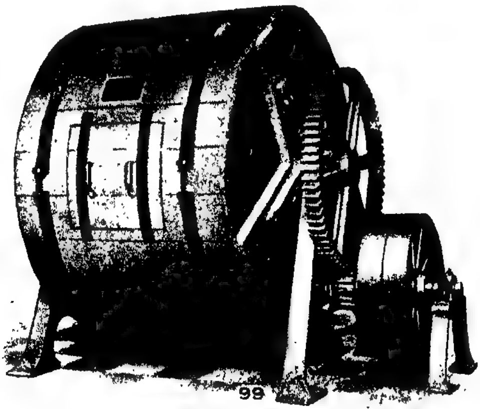

FIG. 20.—Rotary Leach.

sides, and the whole connected with a main steam pipe above. The transference of the liquor from one drum to another is effected by means of an overhead trough, into which the liquor is forced. The strong liquor is subsequently clarified, filtered, and passed on to the concentration plant. The spent tan is dropped into trucks, placed below the level of the ground, and run into the furnace.

Autoclaves.—The next system of extraction to be considered is by means of autoclaves, in which the material is extracted under pressure.

The extraction of tanning materials in autoclaves under pressure generally yields a larger total extract than ordinary open vat extraction, but at the same time a certain amount

of tannin is lost, varying with the pressure used. Eitner in some early experiments clearly showed this loss, and a few of his results are given below:—

Pressure in Atmospheres.	Oakwood.		Mimosa Bark.		Valonia.		Myrobalams.	
	Tannin.	Non-Tans.	Tannin.	Non-Tans.	Tannin.	Non-Tans.	Tannin.	Non-Tans.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
1	6.44	3.32	31.61	10.49	29.97	19.26	25.02	16.12
2	6.50	4.46	30.75	13.54	27.28	23.42	23.02	21.17
4	5.52	18.08	29.98	14.25	24.78	23.41	14.52	31.46
6	2.57	22.34	26.60	14.73	18.92	22.53	12.49	31.63

Since Eitner's work, Paessler has made further determination regarding the effect of increasing the pressure on the tannin yield (*Collegium*, 1913, p. 88). His results for chestnut wood are as follows, the figures being calculated on the basis of the wood used, containing 14.5 per cent. of moisture:—

Pressure in atmospheres	1	3	3	5	7
Duration in hours	...	1	2	1	1
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Tannin	7.1	7.0	7.1	6.4	4.4
Non-tannins	3.9	5.4	7.5	11.9	20.1
Monosaccharoses	1.0	1.1	1.4	2.2	6.0
Disaccharoses	0.3	0.6	1.3	4.2	8.3

Autoclaves are expensive in first cost, as, for the purpose of tannin extraction, they are made entirely of copper, and one would not adopt them unless for the extraction of materials low in tannin. It is not clearly established as to whether this destruction of tannin matter is the immediate effect of increase in pressure or increase in temperature, due to the higher pressure used. It is generally concluded, therefore, that pressure extraction yields a higher amount of "total extract" than is obtained by the open leach method, but the product is darker in colour and contains a higher proportion of non-tannin substances.

A battery of pressure autoclaves is shown in Fig. 21.

It will be understood that these autoclaves are made of copper, and therefore their installation entails a large initial outlay of capital. For filling and emptying respectively, a hinged door is arranged at the top and bottom of each autoclave, while heating is done by direct steam. The steam is blown into the liquor until about a 30 lbs. pressure is reached.

Vacuum Leaching.—The extraction of tanning materials under reduced pressure is the basis of the Nance process, an account of which has been published by Hough (*Le Cuir*, 1919, No. 14), although the results of small scale workings only are described. However, it is expected that in

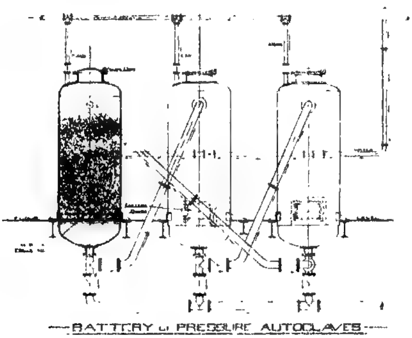

Fig. 21.—Battery of Autoclaves.

vacuum extraction practically no decomposition or discoloration takes place, and provided the yield of extract is good, the method strikes one as presenting distinct advantages. In the work by Hough, the extraction of the material (mimosa bark) was made at a temperature of 32° C., and 75 per cent. of the total tannin was extracted with three waters at the rate of 90 litres per 25 kilos of bark. The method is as yet in its infancy, but is one from which much might be expected.

Roller System.—This is the process patented by Bilbrough and Frew, an outline of which has already been given (see p. 54).

Open Trough and Screw ("Automat" apparatus).—This consists of a long wooden trough, in which is fixed a copper and brass Archimedean screw. The bark is fed in at one

end and carried forward by the screw, meeting the water counter-current, which is admitted from the other end of the trough. When extracted, the bark falls into a hopper and is carried away by elevators. Clogging is the main drawback to this system, but it has been known to give excellent results with many materials without any attendant difficulties. Careful observance of the time element and regulation of the quantity of leaching water are of great importance in order that a maximum of extraction shall be secured.

Gas Agitation Process (Fraymouth-Reavell-Kestner Evaporator and Engineering Co. Patent).—It has already been mentioned that too fine grinding of the tanning material will invariably lead to clogging in the leaches, but the process of extraction now under discussion allows of the treatment of very finely ground material. It was during an investigation on the tannin barks of India at the Esociet Tannin Research Factory, Maihar, 1916-20, that the problem of treatment of non-fibrous and dry barks (containing only 5 per cent. moisture, which crushed with ease to a fine powder) was solved by the invention by Mr W. A. Fraymouth, of a gas agitation process in which the fine subdivision of the tanstuff is a positive advantage.

In this process the principle applied is similar to that of the Pachuca tank which has been so successful in wet metallurgy. In order to prevent oxidation of the liquors, Mr Fraymouth uses the exhaust gases from a charcoal gas engine, which can be fed with charcoal derived from the spent bark powder, thus making for great economy. It is interesting to note that the very small amount of creosotic gases, which come forward from the engine, have the effect of stopping fermentation in the tannin liquors from the first moment of solution, with consequent saving of tannin. After small experiments, a plant on a practical scale (4-5 tons of bark per charge) was constructed at the cost of the Indian Munitions Board at Maihar. Six cylindrical vats of teakwood with conical bases of glazed brick were found sufficient to completely extract the tannin from a long series of different tanstuffs submitted to the process. In many cases the extraction was complete in less than six vats. At first it was found difficult to get quite clear liquors, but the introduction of annular veils of jute canvas behind which the liquors must rise through 20-30 ft. of column, slowly settling out all solid matter, obviated this difficulty. Later, an automatic device for the charging and wetting of the

powdered bark and final strengthening of the liquors completed a process which (*a*) automatically handles the bark from a mill and grading plant, charging it through a wetting vat into the leaches or agitators; (*b*) extracts at once the bulk of the tannin, while wetting the powdered bark, and thus delivers liquors of much greater strength than those from ordinary leach-pits to the evaporators; (*c*) passes the half-exhausted tanstuff to a system of agitators from which the finally completely exhausted spent tannin is automatically discharged to waste or to by-product plants. As to the spent tannin, we have never been able to extract more tannin at the same temperature in the laboratory from given samples of extracted pulp.

Mr J. Arthur Reavell, of the Kestner Evaporator and Engineering Co. Ltd., and his staff have recently collaborated with Mr Fraymouth in perfecting details of the process, and in the design of a large scale plant which is being erected in Central India. The illustrations (Figs. 22, 23) show the block of agitators set in a ring around the central wetting vat.

The central tanstuff wetting agitator consists of a cylindrical vat A of wooden staves, bound together at close intervals with galvanised round iron bands, which can be tightened at will. This cylinder is set in a masonry base F, to which it is tied down by bolts and anchor plates into a circular channel. Within this vat are placed four "uplift" tubes, B, B, B, BS, of wood. The bottoms of these tubes are open on all sides to admit the pulp, *i.e.*, powdered tanstuff and liquor. Each is fitted with a bronze gas pipe H running down the centre, having a valve at the bottom to permit of delivery of non-oxidising gas at the bottom.

The tops of these "uplift" tubes are fitted with three removable return bends, interchangeable with a swan-neck bend. Three of the bends, B, B, B, simply direct the stream of pulp back into the centre of the vat A, while the one bend, BS, is made long enough to extend over the edge of the centre vat A, and to discharge into the centre of any one of the outside agitators. The bend on BS can be fitted to any one of the four "uplift" tubes, and thus each of the eight agitators can be fed from the centre vat. The underside of the bend on BS is perforated at D to allow a part of the liquor to pass back over a shoot E into the second annular zone J, while the partly drained tanstuff pulp passes down the long shoot into one of the agitators in the outside ring.

These four "uplift" tubes are bound together with a ladder-like wooden framing, all of which composes a square

frame which stands by itself on the bottom of the centre vat. The outside of this framing is covered with jute canvas, which we term the "inside canvas veil," and this is to prevent fine slimes from passing horizontally from the inside outwards (jute canvas rapidly becomes impervious to liquors in the vats). This "inside canvas veil," which is open all round at the bottom, and extends upwards to about the height of the underside of the bends B, B, B, forms an inner tanstuff-wetting zone J.

Outside this veil Q, and attached to the walls of the vat by brackets and suspended from a ring of bamboo, hangs another veil Y of jute canvas. The top of this veil Y extends to a point slightly lower than the top of the walls of the vat, so as to permit the shoot E to slope back into the second annular zone J. The veil Y reaches to within a short distance of the bottom of the vat, and it should be so placed that it stands at equal distance everywhere from the walls of the vat, but may be arranged to stand away from the top of the vat, and thus afford a first annular zone K of greater cross-section area at the top than at the bottom. The veil Y is provided with screens V, V at the bottom to prevent from rising such articles as are difficult to wet. There is always a small proportion of corky matter which will not wet.

It is essential that this first or outer annular zone K should be quiescent and allow the liquor to rise very slowly upwards through a high column of liquor until it reaches a knife-edge launder L, attached to the walls of the vat. This launder L is set or shaped to be exactly level all round, so as to cut off only the completely clarified top layer from the first or outer annular zone K.

The agitators in the outer ring are all similar, and are set at a level which is somewhat lower than the centre vat A. There is an average of level between the top of the liquor in the outside vats and the top of the liquor in the inside central vat A of 4 ft. 6 in.

Each of these agitators consists of a cylindrical open vat built of wooden staves and a conical base of masonry. The bases of the wooden cylinders are set in circular channels, and are tied to the masonry in the same manner as the centre vat A.

A centre "uplift" tube N of wood is placed in the middle of each of these vats and reaches down to within a short distance of the bottom of the cone. Down the centre of each of these central "uplift" tubes M is led a bronze pipe N which leads compressed gas to escape through a valve O.

Outside the centre tube N, and attached to the walls of the vat, is hung a cylindrical veil R of jute canvas, which is attached to a ring of bamboo on brackets well above the top of the walls of the vat. The bottom of this veil R, at the point where the cone joins the wooden cylinder, is provided with screens W to prevent the unwetted material mentioned above from rising through the quiescent zone U between the veil R and the walls of the vat. Each of these agitators is provided with an inflow pipe G, which passes through the walls of the vat and the canvas veil and feeds liquor into the agitation zone. Liquor passes out of the vat in a similar manner to that described in connection with the central tanstuff-wetting vat A, namely, over an annular knife edge launder (not shown in detail), and out of a pipe leading from this to a connection which leads into the inlet pipe of another agitator. These connections are of flexible hose, with couplings to permit of connection between any two agitators in the ring. This arrangement permits of throwing out any given agitator for repairs, etc.

The bottom of the conical base is provided with a pipe and siphon leading past cock P discharging to waste, so that the whole contents of an agitator, exhausted tanstuff and water, can be run off.

A pump is provided which can be attached at will to any one of the vats which will lift strong liquor and deliver it into the central tanstuffs wetting zone of vat A.

The *modus operandi* is as follows:—

Assuming the whole plant to be full of wet tanstuff and liquor and that the gas has been turned on, thus keeping all vats in constant agitation, and one of the outside agitators full of exhausted tanstuff and water, practically all tannin having passed away. The cock P on this agitator is then opened and the contents of the vat or its settled sludge run to waste or to spent-tan driers and consumers.

We will suppose this vat to be No. 8. Plain heated water is now allowed to flow into No. 1 vat. If all the vats are connected in series the head thus produced in No. 1 vat will cause the displaced liquor to flow from No. 1 into No. 2, from No. 2 into No. 3, and so on until the richest liquor flows into No. 8. As soon as No. 8 is full of liquor the bend BS is fixed on the "uplift" tube in vat A nearest to Nos. 7 and 8, when newly wetted tanstuff and some strong liquor will pass into No. 8. As this displaces liquor, the latter is pumped into the centre tanstuff-wetting zone and fresh powdered tanstuff may be added as follows:—Between

the mill and the centre tanstuff-wetting vat A is placed an impelling fan, and the dry powdered tanstuff is transported through a bellmouth pipe to below the surface of the liquor in the central tanstuff-wetting zone of the centre vat A. The compressed gas having been turned on in all four "uplift" tubes very large quantities of pulp consisting of strong liquor and wetted tanstuff are drawn from the bottom of vat A. Three-quarters of this pours back on to the top of the liquor, thus sucking down and swamping the dry powder. Attention must be drawn to the fact that the whole contents of the centre zone is now travelling downwards rapidly and is being thrown up again under incessant mixing and agitation. Not only is the finely powdered tanstuff thoroughly wetted and allowed to swell, but a very large proportion of the available tannin is yielded to the liquor, which was rich in tannin before. It will be found that it is possible in this way to obtain much richer tannin solutions than by any other process. Our liquors have shown upwards of 20 per cent. of solid matter on evaporation.

It should be mentioned here that water of the desired heat can be used at the start of the process and liquors may be reheated before passing from the outside agitator containing the richest liquor, and before they are discharged into the tanstuff-wetting zone. We have found by experiments that every tanstuff has its own critical temperature at which it yields suitable tannin to water or tannin liquor.

One-quarter of the uplifted pulp is thrown by the force of the gas into the bend BS, and as it passes along this bend some of the strong liquor passes through the perforations D, back along shoot E, into the second annular zone J. This liquor contains fine slime at this stage. The solid matter (wetted tanstuff) passes down the bend BS into the agitation zone within the canvas veil of No. 8 outside agitator. Here it is violently agitated with the liquor passing from No. 7 and produces strong liquor which is pumped into the centre vat A, as above described.

The unclarified rich liquor which passes into the second annular zone J passes slowly to the bottom of vat A, and rises slowly up the first annular and columnar zone K, dropping all its suspended matter, until it reaches the knife-edge launder L over which it passes as a clear liquor heavily loaded with tannin. It may be lifted after this if desired and passed either to tanning pits or to an evaporating plant for concentration.

As soon as No. 8 vat has received its full charge of

wetted tanstuff it will be found that No. 1 vat, having received a large supply of heated water during the above operations, now contains only traces of soluble tannin.

The liquor in No. 8 vat is now pumped into the central vat for use, fresh water is now added to vat No. 1, which causes the liquor to flow from No. 7 to No. 8, No. 6 to No. 7, and so on. When sufficient of this water has passed into No. 1, its whole contents may be discharged to waste, although in practice it is possible to stop agitation for a time and to discharge the thickened pulp or sludge, leaving much of the clear water in the upper part of the agitator ready for the next charge. During this periodic change, the feed of crushed dry tanstuff may be stopped, and the flow of heated water and the pump from the outside agitator with the richest liquor to the central tanstuff-wetting vat A may be stopped also, but agitation by gas continues in all vats, so that the process of washing out the tannin is continuous.

After emptying No. 1 vat and after sufficient of the liquor from No. 8 vat has been pumped into vat A, No. 1 vat is loaded with liquor and fresh wetted tanstuff as above described, and so on similarly with other agitators as and when their contents are sufficiently exhausted of tannin.

The process is primarily designed for the large scale production of tannin extracts and not for application in the tanner's yard, but the inventor has worked out an application of his ingenious settlement columns behind canvas veils, which is simple to apply in the ordinary tanner's leaching plant. The advantage to the tanner of being able to separate all bark dust and to use this to strengthen his liquors, while his leach pits would contain only fibrous bark, does not need description.

Mr W. A. Fraymouth has conducted a series of experiments which demonstrate clearly that, in most fibrous barks, the tannin is not contained in the fibres, but in the non-fibrous cementing medium between the fibres. Most tanners know that the dust from crushed bark is rich in tannin, but few realise that a mimosa bark carrying 32 per cent. tannin yields dust which carries 46-48 per cent. tannin. So long as the original bark is quite dry—a condition, it is true, difficult to produce in Europe—a fibrous bark may be passed through a mill with a blower below, which allows almost tannin-free fibre to fall below the mill and drives the dust further down a tunnel, where it can be found as a bark dust rich in tannin. A bark containing 7 per cent. tannin has been made to yield a 32 per cent. dust and to leave only

1½ per cent. tannin in the fibre. This clearly indicates the proper way to treat fibrous barks in countries where the bark can be handled dry, and perhaps it would pay in Europe whenever it is possible to thoroughly dry the bark. A large proportion of the bulk of the bark as fibre could be rejected, while the rich dust could be treated by the gas agitation process.

Spent Tan.—This spent material from the extractors is drained as far as possible of its moisture, and is then conveyed to the boiler furnaces to be used as fuel. It is, of course, necessary to use proportionately larger grate area in the furnaces to compensate for the lower calorific value of this class of fuel as against coal. There are a number of types of furnaces which have been designed to meet these requirements, but the main point is to have as much fire-brick as possible surrounding such furnaces, so that the reflected heat dries off the moisture from the material, rendering it of higher combustible value as it descends on the fire grate. Waste bark has also been employed in the manufacture of brown paper, and recent work has shown that, provided the correct methods be used, a very good white paper can also be made. Other uses to which spent tan can be put are many, and include lino making, but it is to be borne in mind that it may be found more economical to burn it and thereby save cost of handling, and at the same time effect a saving on the fuel bill.

Clarifying and Decolorising.—The liquor as it leaves the extraction vats should contain up to 10-11 per cent. of dissolved solids, the tannin content, of course, varying with the composition of the raw material. It has next to be clarified and if necessary decolorised.

The treatment given will depend largely upon the nature of the liquor, for example, mimosa liquors rarely want decolorising but simple filtration to get rid of such insoluble matter as bark in suspension. On the other hand, other liquors require to be decolorised to some extent in order to lighten the colour. The liquor is pumped into large settling tanks and there decolorised if necessary by chemical means, and then filtered.

Filtration can be done by any of the following processes:—

(1) Simple sedimentation.
(2) With filter cloths over wooden frames.
(3) By filter presses.
(4) By centrifuging.

The first two need little description and the necessary plant can be arranged to meet working conditions.

Filter pressing is a very satisfactory method of filtering

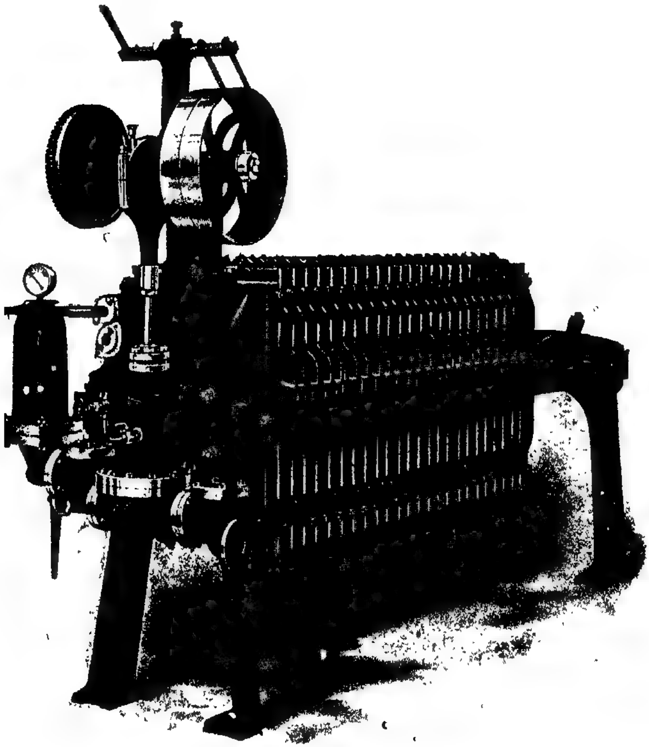

FIG. 24.—Filter Press. (S. H. Johnson Ltd., London.)

tan liquors and is largely employed for this purpose. A typical design is shown in Fig. 24.

In order to avoid contact of the liquor with iron, the plates of the filter press are constructed of wood and the pump of brass. The passages through the cast-iron head of the press are also lined with brass so that there is no contact

with iron in any part. The feed pump may be either belt driven as shown in the illustration, or if more convenient a steam pump of the direct acting type may be substituted.

In addition, the press shown in Fig. 24 can be fitted with self-contained electrically-driven pumps; the motor and

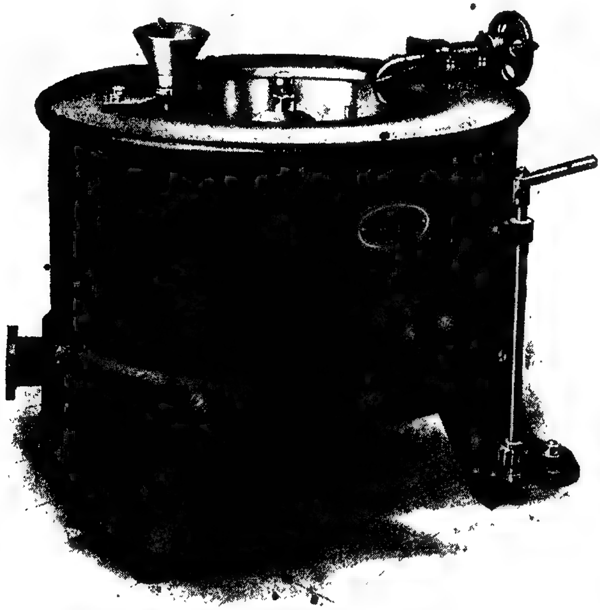

FIG. 25.—Broadbent Centrifuge for Separating Fine Solids in Suspension.

speed reduction gear together with the pump being mounted self-contained on the head of the filter press.

Clarification by Centrifuges.—Where the question of rapidity, together with uniformity of liquor, is desired, there is no doubt that the use of the centrifuge for clarification is most efficient. A type suitable for extract work is shown in Fig. 25, while a section of the machine is given in Fig. 26.

The arrangement of a centrifuge for tan liquor clarifica-

tion is somewhat different to that used for the separation and drying of crystals, etc., inasmuch as the usual wire basket is replaced by an imperforate rotating cage, on the side of which the insoluble matter is collected. Also, a number of radial baffle plates are inserted to prevent bad vibrations, etc.

The liquor is fed in through the funnel device shown, and

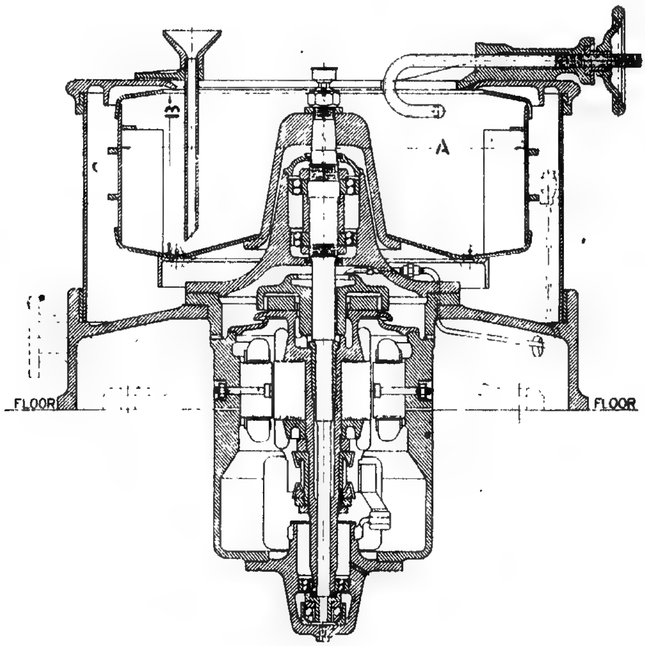

FIG. 26.—Broadbent Electrically-Driven Centrifuge for Separating Fine Solids in Suspension.

the clarified liquid finds its exit through the adjustable skimmer pipe attached to the pan top. The solid matter is forced on to the cage side, from whence it is scraped after a thick layer has been formed. It is important to note that by this method of clarification no darkening of the liquor occurs.

Decolorising.—The decolorising of tannin solutions is a matter which has received considerable attention and has been the subject of numerous patent specifications. Oxalic

acid was suggested by Coëz (E.P. 3,150, 1883) who used it in conjunction with gelatinous alumina. One gm. of oxalic acid per 100 litres of liquor was first added and then 250 gm. of gelatinous alumina. The alumina is undoubtedly the essential agent. The use of this material in another form (activated alumina) has been patented by Arnoldi and Freiberg School (E.P. 19,804, 1909). The alumina is prepared by washing aluminium with caustic soda and then treating the cleaned metal with mercuric chloride solution. Barium aluminate can also be used for clarifying (Gesellschaft Tamnum, m.b.H., G.P. 242,483, 1909), and the excess of barium removed by adding a sulphate or sulphuric acid. W. Clarke in E.P. 17,402, 1895, suggests the following process applicable to mangrove liquor:—

After the bark has been extracted with water, the liquor is concentrated to half the original volume and then alum added (other materials are also specified). As an example, 533 lbs. of bark are extracted, and 30 oz. of alum added to the liquor.

Aluminates of the alkaline earths have been stated to give good results (Damkohler and Schwindt, E.P. 24,889, 1909), while these patentees have also introduced a method of electrolysing the liquor, using aluminium and zinc electrodes. Decolorising by the use of metals alone was mentioned by Peyrusson (Addition F.P. 318,523, 1902) who suggested tin foil. About the same time, Fratelli Dufour Co. were granted E.P. 11,502, 1902, for the use of metallic powders, of which the following is an example: 1,000 kilos of quebracho extract (liquid) are treated with 4 kilos of tin powder and 0.2 kilo of aluminium powder, the whole being heated to 100° C. to effect the desired result.

Substances of an albumin-like character have been found very effective in reducing the colour of tan liquors, and the Gondola process involving ox blood is widely used on the Continent. Fuchs and Schiff (*Chem. Zeit.*, 1896, p. 926) state that 1,000 litres of tan liquor can be treated with 0.94 kilo of dissolved albumin and the liquor raised to 60° C. to coagulate. In passing, it is mentioned that 12 per cent. of the total tannin is destroyed, but such a loss appears very considerable and in actual practice is not the case where due care is exercised. Sanford (E.P. 12,450, 1897) uses albumin in conjunction with a fluoride or bifluoride, and the reagents cold, and coagulating by heat; or if preferred, by the addition of picro-acetic acid. Naturally the use of one albuminoid substance at once suggests the use of others—more especially

waste protein matters. In this direction Sinans and Gouin add ½ kilo of oil seed residue to 100 litres of liquor, boil and cool, while Damman (G.P. 274,974, 1913) uses a special preparation known as "Edamin," consisting of the proteins of soya beans. Also, skimmed milk has been proposed (Tillberg, F.P. 395,499, 1908).

The colour-absorbing properties of inert materials have been made use of from time to time, an early specification being that by Marechal and Bories (E.P. 10,147, 1885), who, for each 1,000 litres of liquor, make the addition of 2 kilos of lead carbonate and 4 kilos of lead sulphate. Sand, clay, kaolin, and barium sulphate were suggested by the Société des Extraits de Chêne en Russe in F.P. 339,064, 1903, and yeast cells after a special treatment, by Clowes and Hatschek.

Another method for clarifying tanning extracts is described in "Bulletin Soc. Ind.," Mulhouse, 1912, p. 69, by Lepetit, Dolffus, and Gansser. The impurities are precipitated by the addition of resin soap solution and barium or lead sulphate. The resin soap and the barium sulphate carry down the impurities. Practical details (*Leather World*, 1912) are as follows:—

Fifteen kilos of resin and 15 kilos of caustic soda solution of 20° Bé. are mixed and diluted to 250 litres; 20 litres of this solution are taken, and 1.7 kilos of 80 per cent. barium sulphate paste, and added to 1,000 litres of the chestnut-wood extract of 2.5°-3.5° Bé.

The mixture is allowed to settle for one hour, when precipitation is complete, the clear supernatant liquor is withdrawn and concentrated, and the deposit is pressed in a filter press.

The method can also be applied to the ordinary concentrated chestnut extract of 28° Bé. For 1,000 kilos of extract take 66 kilos of barium sulphate paste, 14 kilos of resin, and 14 kilos of caustic soda solution (20° Bé.). This is followed by 2 kilos of sulphuric acid of 66° Bé. and 2 litres of water, to restore the acidity. After twenty-four hours, precipitation is complete, and the clear extract is 25° Bé., and is very similar to that obtained by treating the weak decoction of 2.5°-3.5° Bé. This process is also described by Guisiana in *Le Cuir*, 1912, p. 611.

Sulphites, hydrosulphites, and bisulphites have been found very efficient materials more from the point of solubilising extracts than as decolorising agents. It is thought convenient, however, to discuss them here.

In 1884 Dontreleau introduced treatment with a sulphite

or hyposulphite, boiling with the chemical added at the rate of 1 gm. per litre of 2° Bé. liquor. Incidentally, aluminium hyposulphite was recommended as being the best for the purpose. Then began the well-known work of Lepetit, Dolffus, and Gansser on the use of bisulphites, resulting in the publication of their English specifications, 8,582, 1896, and 2,603, 1898. The first patent mentioned the use of bisulphites and neutral sulphites with hemlock and quebracho, while the second, more comprehensive, states that soluble quebracho extract can be made by heating the material with alkaline substance, either with or without the further addition of sulphites, bisulphites, formates. Hydrosulphites of alkaline earths, zinc, or aluminium are also mentioned.

Another method of solubilising is given in a patent by Kleink (E.P. 26,063, 1901), this being more suitable for the treatment of extract. The extract is first treated with aluminium sulphate and then with sodium bisulphite, forming sulphur dioxide *in situ*, thus:—

$$Al_2(SO_4)_3 + 6NaHSO_3 = Al_2(OH)_6 + 3Na_2SO_4 + 6SO_2.$$

For 5,000 litres, 4 kilos of aluminium sulphate and 15-20 kilos of 40° Bé. bisulphite are required, and after being allowed to settle, the extract is evaporated to a water content of 20 per cent. (U.S. Patent).

According to Dufour, the solubilising effect of bisulphites is increased in the presence of formaldehyde, and at a later date (F.P. 362,780, 1906) the Badische Anilin und Soda Fabrik patented the use of Rongalite C., suggesting 5 gm. of the reagent for each litre of 4° Bé. liquor, either alone or in conjunction with formaldehyde bisulphite compound. Redlich and co-workers have also brought forward a number of methods for solubilising quebracho, and their results are embodied in E.P. specifications, 4,358, 1908; 16,527, 1911; 7,389, 1912. In the first method, liquors of 12° Bé. taken from the leaches are boiled under pressure with the exclusion of air. After cooling, the flocculent precipitate can be easily separated off. This process has the advantage that no chemicals are used. In the second process, liquors are allowed to settle and the sludge dissolved by heating with caustic soda or potash for seven hours, using one part of alkali for each 1,000 of original liquor. The red solution formed is subsequently used for clarifying.

The third method for the manufacture of soluble quebracho extract is by means of centrifugal action (*Leather World*, 1912). As is well known, one difficulty with quebracho

extracts, is the presence of the phlobaphenes. These phlobaphenes are almost insoluble in water and in weak tanning solutions, and when extracts containing such phlobaphenes are added to tan liquors there is a deposition of the insoluble reds.

The solubility varies with concentration and temperature —that is, it rises with increasing concentration and temperature. Use is made of this fact in the present invention to get rid of the objectionable phlobaphenes. The extract is subjected to centrifugal action, so that the insoluble portion, having a higher specific gravity than the liquid, is driven to the periphery and can be separated. The special point about the patent is that the temperature and the concentration at which the centrifugal action is carried out are varied according to the special purposes to which the extract is to be put. For example, if the extract is required for drum tanning, the centrifuging is carried out at a temperature of 30°-40° C., whereas if the extract is required for liquor tanning, the centrifuging is done at a temperature of 10°-15° C.

In conjunction with Wladlika, Redlich also suggested heating the extract *in vacuo* with an alkaline carbonate for two hours, cooled, and the equivalent of acid added. The resinous substances can then be separated off by sedimentation.

Prolonged cooling has recently been said to be effective for clarifying, and by cooling to 14° C. or below for a certain time the liquor can be freed from much non-tannin (G.P. 323,135, 1916).

Many other methods have, from time to time, been invented, but of these only mention need be made.

1. The use of strontium salts (E.P. 7,106, 1891).
2. Sodium ferrocyanide (E.P. 8,604, 1893).
3. Electrolysis of the liquor to which oxalic acid and salt have been added, using electrodes of platinum netting (E.P. 4,385, 1891).
4. Addition of chromium salts (F.P. 383,890, 1907).
5. Addition of nicotine, either alone or with linseed mucilage, and heating to 55°-70° C. (E.P. 20,680, 1898).
6. It has been observed by Sommerhoff (*Collegium*, 1913, p. 484) that the addition of warm sugar solution clarifies, but darkens the colour.
7. It is claimed that the addition of synthetic tannin also brings about clarification of liquid extracts.
8. Sulphur dioxide is used, and is either blown into the liquor or sulphur boxes adopted, through which the liquor descends in a fine spray, meeting the SO_2 in counter-current.

One disadvantage of this process is that the acid has a tendency to eat into the metal fittings of the apparatus.

In some instances tanners take it upon themselves to decolorise their own extracts, buying dark products and then decolorising them according to their own ideas and with what materials they consider best. For this purpose the plant shown in Fig. 27 is known to give exceedingly good results.

Effect of Sulphited Extracts on Leather.—When sulphited extracts were first put on the market the point arose as to whether the SO_2 contained in them would have any harmful effect on the leather fibre. The point was thoroughly investigated in the first instance by Parker and

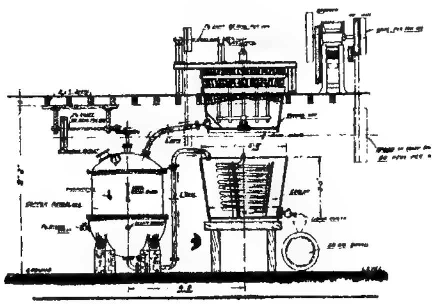

FIG. 27.—Decolorising Plant.

Gansser who held the view that no ill effect would result. On the other hand, Paessler contends that sulphited extracts give rise to sulphuric acid in the leather, and gives results showing how sulphuric acid is at least formed in the liquor made from these extracts.

A sulphited quebracho liquor of 2° Bé. was allowed to stand for some time, when it was noticed that the smell of SO_2 gradually disappeared and the sulphuric acid content of the liquor rose from 0.006 per cent. to 0.265 per cent. In a later publication by Lepetit and Gatta (*Collegium*, 1904, 311) the view of Parker and Gansser is upheld, and they say that free acid is not formed but sulphates. In the light of the fact that enormous quantities of sulphited extracts are now used (bleaching extracts) there would appear little cause for alarm on the matter.

Evaporation.—The liquor, after clarification, has next to be concentrated in order to remove the greater part of the

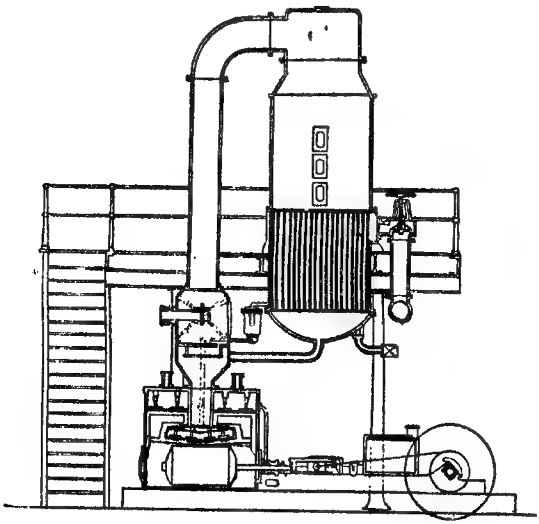

FIG. 28.—Single Effect Evaporator.

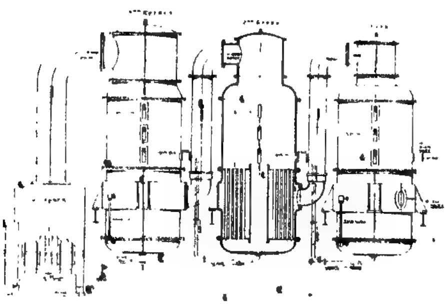

FIG. 29.—Triple Effect Evaporator.

water. As is known to most readers, it is not advisable to concentrate tan liquors in open pans. In order to secure a low temperature at the correct stage of the evaporation

process, vacuum evaporators are adopted. They are of different types, including the following: vacuum pans of the

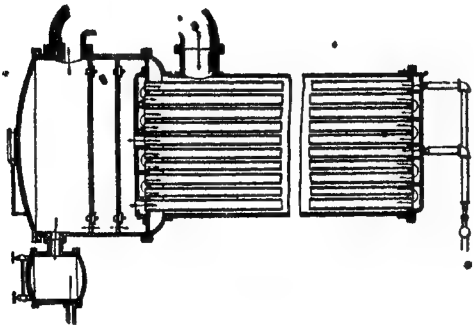

FIG. 30.—Yaryan Evaporator.

calandria pattern as largely used in sugar manufacture, and evaporators operated on the film principle.

A single effect evaporator is shown in Fig. 28, and a triple effect in Fig. 29.

As distinct from the usual vacuum pan, we have also evaporators of the "film" type, namely the *Lillie* evaporator, the Yaryan evaporator, and the "Multiplex," which is a multiple effect evaporator with the different calandrias superimposed. A section of the Yaryan is shown in Fig. 30.

With the plant, the liquid to be evaporated is circulated inside the tubes, with the heat outside. From a technical standpoint, however, the horizontal film evaporator has many disadvantages which are absent in the most modern form of plant, such as the Kestner patent climbing film evaporator, a unit of which is shown in Fig. 31, and a series of these in Fig. 32.

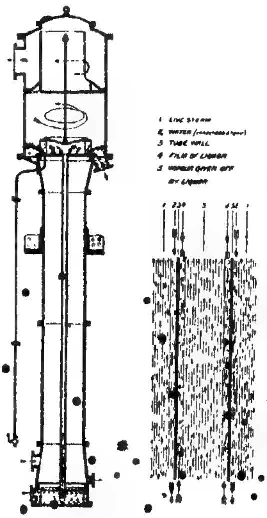

FIG. 31.—Kestner Patent Climbing Film Evaporator.

In the climbing film evaporator the liquid is fed into the tubes from a tank about 3 ft. above the bottom tube plate, or a pump is used, and assuming that this liquor is hot, ebullition at once takes place, on steam being applied to the outer surface of the tube, releasing a large amount of steam, which must find its way to a region of lower pressure by passing up the tube. This is the basis of the climbing film. The liquor and vapour on leaving the top of the tubes meet a fixed centrifugal baffle, where the liquor

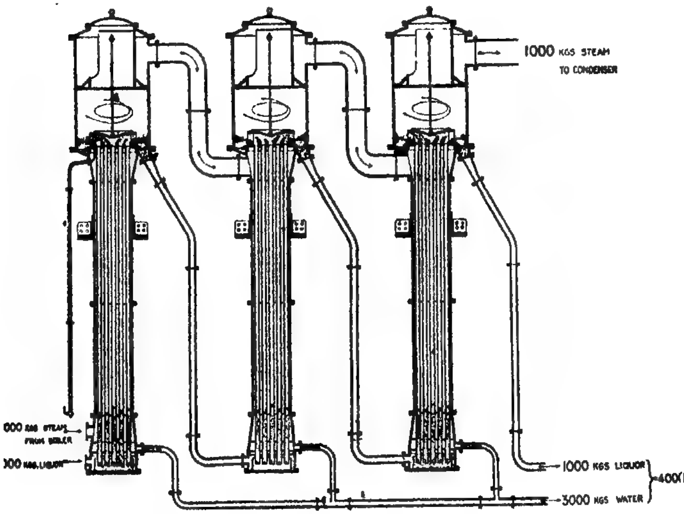

FIG. 32.—Kestner Patent Climbing Film Evaporator in Triple Effect.

is separated from the vapour, the former passing to the concentrated liquor tank, and the latter to the atmosphere or the condenser. The working of a triple effect, of course, renders the evaporation far more economical than with just a single effect, because approximately in a single effect evaporator there is required approximately 1 lb. of heating steam for an evaporation of 0.9 lb. of water, whereas with triple effect 1 lb. of steam would evaporate about 2.2 lbs. of water for the same fuel consumption.

An improvement has been made quite recently in the processes of evaporation by the firm, Prache & Bouillon,

of Paris, with the result that a simple effect apparatus of their design, working at atmospheric pressure, is equal in efficiency to an ordinary quadruple effect working with vacuum.

One of the most important parts of this installation is that which is known as the "thermo-compressor." The thermo-compressor is of the injector type, without moving parts; it is always primed, and cannot get out of order. The object of the thermo-compressor is to draw the ebullition steam arising from the liquid under concentration, and to compress it; this steam thus compressed and raised in temperature according to the density of the liquid to be evaporated, passes into the heating chamber of the evaporator, where it is condensed after evaporating a further quantity of water.

The power necessary for the compression of the ebullition steam is produced by extracting the dynamic energy from the live steam at high pressure. Part of the ebullition steam passes into a reheater, raising the liquid to be concentrated to its ebullition temperature before it enters into the evaporator.

Briefly, in a Prache & Bouillon evaporator:—

(1) The ebullition steam from the liquid is revitalised.

(2) The ebullition steam is compressed by expanding a certain quantity of live steam in the thermo-compressor. Until now the energy in steam has been imperfectly utilised, even in multiple effects, for, in multiple effects, live steam at boiler pressure has not been used.

(3) The preheating of the liquid to be evaporated is effected by the transference of heat units from ebullition steam, which heat units were derived originally from the live steam.

In such a cycle of operation, the whole of the energy of expansion and the heat energy in the live steam are utilised.

The compression of ebullition steam can only be of value if the work of compression is small.

With this end, Messrs Prache & Bouillon have designed apparatus working under a very small transference of heat.

The high coefficient of the transference of heat is obtained by:—

(1) Rapid and continuous circulation of the liquid in the apparatus by means of an impeller.

(2) An arrangement by which the heating surfaces are self-cleaning.

Thus, the Prache & Bouillon evaporator, fitted with the

thermo-compressor, effects a very great reduction in the amount of steam used.

The evaporators already described are adapted for the production of liquid extracts. In the case of solid extracts a different type of "finisher" is necessary, and one of the main difficulties in the making of solid extracts is the lack of circulation of the material during further evaporation. To overcome this defect as much as possible, use can be made of the apparatus shown in Fig. 33.

This contains a series of short tubes from 3-5 ft. long expanded into the upper and lower tube plates. In some cases also a large central tube is built. The circulation is effected by the Archimedean screw seen on the left.

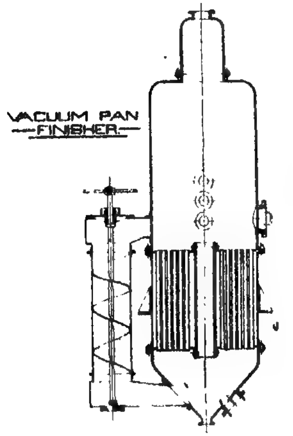

FIG. 33.—Vacuum Pan Finisher (Kestner).

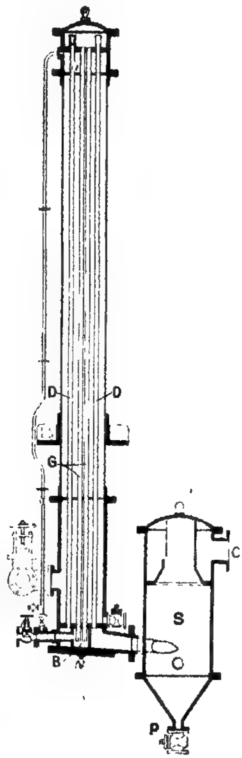

FIG. 34.—Evaporator for Solid Extracts.

Modifications of this plant can be and are made to suit requirements.

Another type of plant for producing solid extracts is that shown in Fig. 34.

Here the liquor is brought near to the boiling point, so that the moment it enters the climbing film tube, evaporation takes place and the usual film action begins. The liquor is carried up the climbing film tubes, descends down the falling film tubes, returns up the climbing film, and finally goes down the falling film tubes into the separator at the bottom. The vapour is passed into the atmosphere, and the thick extract run into bags where it solidifies almost immediately.

With the vacuum pan finisher, a large body of extract is held in the pan for a period varying from ten to twelve hours, but owing to the fact that concentration is conducted under vacuum at a low temperature, the finished extract is drawn off direct into bags. In the Kestner finisher the temperature for final concentration is high, being approximately 100° C., but the time of contact is only a few minutes and does not appear to influence the quality of the extract.

A number of processes have been introduced for the preparation of tanning crystals. One such process has been described by Smaic and Wladlika, the following abstract of which is taken from the *Leather World*. The process is the same as is used for the preparation of milk powder, dried blood, eggs, etc., substances very prone to decomposition when heated for any length of time at a high temperature.

It consists in principle in the projection under pressure of a finely divided spray of the liquid to be desiccated into a closed chamber, the latter, so arranged that the water vapour given off is continuously withdrawn. As the result of the projection of this very fine spray, the particles present a large surface for evaporation, with the result that desiccation can be carried out at a comparatively moderate temperature.

The evaporation is also helped by the introduction of hot air, and this again can be so regulated as to control at will the moisture content of the dry powder formed. The hot air is completely dried before being passed into the chamber.

The dry powdery extract so obtained falls to the bottom of the chamber, on an inclined base, so arranged as to be easy to remove. In the erection of a drying plant a spacious floor space is an essential, the drying chamber being 50 sq. m. and 4½ m. high. The plant required consists of an air filter, an air compressor with a compressed air chamber, a spraying

apparatus and an apparatus for exhausting from the chamber the water-saturated vapour.

As regards the actual working of the plant, experiments have shown that liquors of a density of 8°-10° Bé. will give

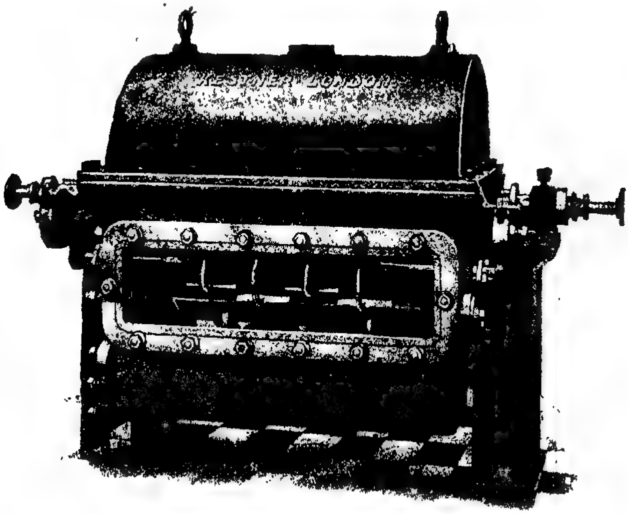

FIG. 35.- Rotary Dryer.

a satisfactory dry powder of a moisture content of from 5-8 per cent.

The advantages offered by this method of concentration and drying are :—

(1) The chemical character of the material is unaltered, *i.e.*, the relation of tannin to non-tannin remains the same.

(2) By one single operation a liquor is converted into a dry extract in a fine powdery form of a low moisture content.

(3) The extract is not hygroscopic, and has no tendency to cake when stored.

(4) Packing is a simple process, and there is a considerable saving in freight charges for transport, while warehouse floor space is saved.

An example is shown in the original paper of results obtained by this method, as follows :—

	Liquor.	Resultant Extract.
	Per Cent.	Per Cent.
Tannin - - -	9.12	50.54
Non-tannins - -	6.99	39.91
Insoluble matter -	0.44	1.97
Water - - -	83.45	7.58
	100 00	100.00

Showing that practically no loss through decomposition takes place.

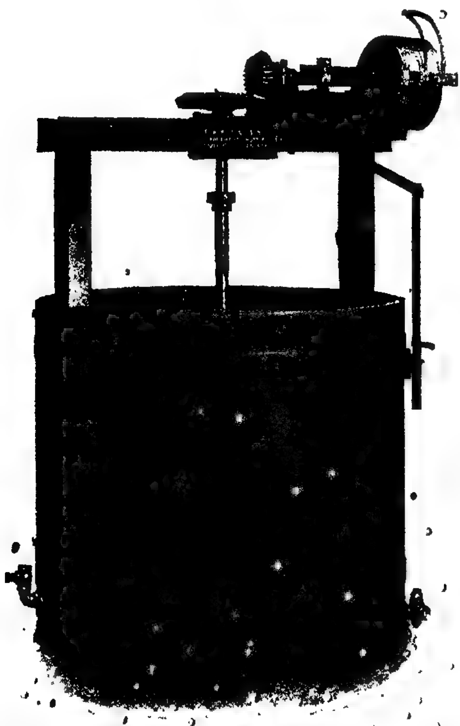

FIG. 36.—Apparatus for Dissolving Solid Extracts. (E. Wilson.)

Another type of plant available is the rotary dryer, an illustration of which is shown in Fig. 35.

A central drum, steam heated, runs in a bath of freshly concentrated extract, which forms in a film on the surface. As the drum is revolving *in vacuo* at a low speed, the material dries on the drum and is scraped off at a point just before the drum goes back into the liquor. These crystals fall to the bottom from where they can be periodically collected.

Redissolving of Solid Extracts.—It has been found by many tanners that certain difficulties present themselves when solid extract is dissolved in water for the preparation of liquors. A special type of apparatus designed to give a uniform liquor is shown in Fig. 36.

This apparatus is made in two sizes, to hold 500 gals. or 800 gals. It is constructed of well-seasoned timber, and all joints tongued and grooved and held together by two strong bands with tightening screws. The vat is fitted with a false bottom on which the extract rests, underneath which the propeller revolves. This propeller is made of gun-metal with hardwood blades fixed at an angle so as to throw the liquor against the underneath side of the false bottom. The shaft to which the propeller is fixed is sheathed with brass, and revolves in a gun-metal step bearing with lignum vitæ block.

The vat is fitted with a gun-metal silent heater, with steam valve attached, and a gun-metal draw-off cock is also provided. All bolts, nuts, and metal fittings liable to come into contact with the liquor are made of gun-metal, so that no discoloration of the liquor can take place.

SECTION II

TANNING MATERIALS

SECTION II

TANNING MATERIALS

A

Abu-Surug (*Prosopis oblonga*).

This bark, from the Sudan, examined at the Imperial Institute, has the following composition :—

	Per Cent.
Tannin	14.4
Soluble non-tannins	6.8
Insoluble matter	67.7
Moisture	11.1
	100.0
Ash	2.7

and in 1906 was valued at about £2. 10s. per ton. It produces a firm brown coloured leather.

Acacia arabica (see Babool, p. 13).

Acacia Species (Various).

The following are the tannin contents of various acacias from New South Wales as examined by Maiden in 1887.

Botanical Name.	Local Name.	Bark Tannin.	Dry Leaves.
		Per Cent.	Per Cent.
A. sentis	... ...	6.32	...
A. penninervis	Hickory and Blackwood	16.96	...
A. melanoxylon	Blackwood and lightwood	11.12	3.38
A. anema	Mulga	4.78	...
A. anema	Narrow leaf mulga	8.62	...
A. homalophylla	Narrow leaf yarran	9.06	...
A. Oswaldi	Miljie	9.72	...
A. longifolia	... ...	15.34	1.93
A. vestita	... ...	...	15.18

A bark from a tree of the acacia species (? *A. spirocarpa*) indigenous to Uganda showed on analysis at the Imperial Institute:—

	Per Cent.
Moisture	9.61
Tannin	10.37
Soluble non-tannins	5.26
Insoluble matter	74.76
	100.00

Barks from various acacias grown in Queensland are given below:—

Names.	Tannin. Per Cent.
A. Cunninghamii	9.13
A. podalyriæfolia	12.40
A. neriifolia	13.91
A. penninervis	14.49
A. leptocarpa	10.20
A. polystachya	18.20

Algarobilla (Algarobitta) (*Cæsalpinia brevifolia*).

One of the most complete analyses of the pods of the South American plant is by Norton, who gives the following:—

	Per Cent.
Tannin	43.0
Soluble non-tannins	20.0
Insoluble matter	21.9
Moisture	13.5
Ash	1.6
	100.0
Carbohydrates	8.2

It is a pyrogallol tannin, and an infusion of the pods is very liable to rapid fermentation. Its general tanning properties are outlined by Norton in the following paragraph:—

"When used in tanning, algarobilla gives much better weight and greater firmness than is the case with divi-divi. It is also less liable to cause discoloration of the leather. The best grades yield a light coloured liquor, which colours the leather but slightly, imparting a light reddish-yellow tint. After the extract has undergone fermentation it produces a leather of an exceedingly bright colour. Experience has

shown that it gives inferior results for sole-leather and that in general, when employed alone, the leather produced is apt to mould in the sheds.

"It is, therefore, in almost all cases, blended with other tanning materials, its exceptionally high content serving to strengthen the weaker liquors. It is usually blended with myrobalams, divi-divi, quebracho extract, or hemlock extract. In practically all cases it can replace gambier for blending."

Algarrobin (? *Prosopis*, Sp.).

As a tanning material, the extract from the wood of this South American tree has had little or no commercial application. It was first introduced as a dyeing extract for the production of grey, brown, and black shades on textiles. Eachus subsequently examined the material, and found it to have the following composition:—

	Per Cent.
Tannin	45.32
Soluble non-tannins	35.55
Insoluble matter	7.11
Moisture	12.02
	100.00

It was first intimated that algarrobin extract was prepared from the wood of *Ceratonia siliqua*, the "Carob" from which locust beans are obtained, but the probability of this being an error was pointed out by the Imperial Institute, who suggested the "algarrobo" (*Prosopis*, Sp.).

"Alimu" Bark.

This is the native name given in Sudan to the bark obtained from *Ximenia americana*, and according to the Imperial Institute has the following composition:—

	Per Cent.
Tannin	16.90
Soluble non-tannins	6.00
Insoluble matter	67.33
Moisture	9.77
	100.00

Aleurites fordii.

The seeds of this tree furnish the tung oil of commerce. The bark, according to the Imperial Institute, contains 11.9

per cent. tannin, 8.7 per cent. non-tannins, with a moisture content of 12.89 per cent.

Amli Leaves (Avala) (*Phyllantus emblica*).

Guthrie says that these leaves contain 20.3 per cent. of tannin, 19.4 per cent. non-tannins, and 4.4 per cent. moisture. They are used by natives in the Bombay Presidency for tanning. Another analysis shows 16.8 per cent. tannin, 11.9 per cent. non-tannins, and moisture 10.5 per cent.

Angico Vermelho (*Piptadenia rigida*, Benth.).

The bark of this tree, which belongs to the natural order Leguminosæ, is used in Brazil as a tanning material. Its tannin content is said to be about 40 per cent.

Aurantine (see Osage orange, p. 69).

Avala (see Amli, above).

B

Babool (Babla) (Sant.) (*Acacia arabica*).

Both bark and pods are used as tanning materials, the former being used more widely in India than elsewhere.

Bark.—According to Guthrie, the tannin content of the Indian bark varies widely, and may reach as high as 20 per cent. The average of a number of analyses gave:—

	Per Cent.
Tannin	12.4
Soluble non-tannins	8.6
Insoluble matter	71.2
Moisture	7.8
	100.0

The tannin present belongs to the catechol group and resembles oak bark tannin, inasmuch as it gives a blue-black colour with iron salts.

The Sudan bark has been examined by the Imperial Institute, who give the following figures:—

	Per Cent.
Tannin	8.8
Soluble non-tannins	3.4
Insoluble matter	76.3
Moisture	11.5
	100.0

The bark gives a harsh and rather dark coloured leather, but is nevertheless used for the tanning of Indian leathers for home use.

Pods.—The pods of *Acacia arabica* are richer in tannin than the bark.

Some analyses of Indian pods by Pilgrim and Fraymouth are (calculated to dry pods):—

	Collected Green Seeds Removed.	Collected Dry Without Seeds.
	Per Cent.	Per Cent.
Tannin	16.86	19.76
Soluble non-tannins	26.43	27.09
Insoluble matter	56.71	53.15
Colour of ½ per cent. tannin solution—		
Red	...	6.9
Yellow	...	26.0

It is evident that the Indian pods are not so good as those from Sudan, judging from an analysis of these latter made at the Imperial Institute :—

SUDAN "SANT PODS"

	Per Cent.
Tannin	35.4
Soluble non-tannins	14.6
Insoluble matter	39.4
Moisture	10.6
	100.0

A sample of seedless pods (canakie) from Morocco examined by Jalade gave 29.5 per cent. of tannin and 13.9 per cent. of non-tannins. Quite recently a product manufactured from sant pods has been put on to the market under the name of Sant Grains.

The grains, which are obtained from the Sudan pods, are prepared by grinding and sieving the dry pods whereby the larger proportion of the fibrous matter is retained, giving a finely divided powder very high in tanning matters. An analysis of the grains made by the present writer is :—

	Per Cent.
Tannin	53.45
Soluble non-tannins	16.80
Insoluble matter	21.95
Moisture	7.80
	10.000
Ash	6.4
Colour of ½ per cent. tannin solution—	
Red	1.2
Yellow	2.1

The tannin of the pods (or grains) is of a mixed character giving reaction for both pyrogallol and catechol tans.

As regards the tanning value of the grains, it produces a soft, plump, and very light coloured leather, upon which can be subsequently dyed very delicate shades without any deadening appearance. As has already been pointed out, it might in many cases replace sumach both for tanning and retanning purposes, and at the same time presents a good substitute for gambier.

It is owing to the fact that the liquor prepared from the pods is liable to rapid fermentation that its use in India has been very limited. To overcome this, the use

of antiseptics has been tried: 0.3 per cent. carbolic acid, or 0.25 per cent. phenazole (calculated on the weight of tanning material) has been found an effective check to the activities of moulds, etc. When phenazole is used a little acetic acid must be added, as this substance is alkaline in character. Another method of keeping fermentation very low is to regulate the temperature of the liquor, 50° F. being given as a suitable maximum.

It is noted that the manufacture of tanning extract from *A. arabica* is patented by the Soc. Anon. des Matières Tannants et Col. under F.P. 480,300, 1915.

Barbatimao Bark (*Stryphnodendron barbatimam*, Mart).

Barbatimao bark is obtained from the tree *Stryphnodendron barbatimam*, and constitutes one of the richest tanning materials indigenous to Brazil. The tree is of an average size, the wood of which is largely used for carpentry and joinery work. Although found in a number of districts, the trees are most abundant in Minas Geraes. The Belgian Minister at Rio de Janeiro states that the bark has certain medicinal properties, and contains 48 per cent. of tannin.

Barbatimao bark has also been examined at the Imperial Institute (Bulletin, 1907, p. 360), but the results obtained do not appear to bear out the statement as regards 48 per cent. tannin. The actual figures are as follows: Moisture, 13.5; tannin, 27.8; non-tannins, 5.2; insoluble matter, 53.5. This latter authority consider that leather made with barbatimao is of superior quality, and if the material could be imported into England in sufficient quantity a market could be found. Trial plantings of this tree have been made in the late German East Africa.

According to the U.S. Consul at Bahia the inner bark contains in addition to tannin a quinine-like alkaloid. The leaves are also said to contain about 7 per cent. of tannin and 8 per cent. of non-tannins.

Paessler says that the bark gives a bright coloured, fine grain leather (*Collegium*, 1906, p. 135).

Beefwood.

This is the local name (New South Wales) given to *Grevillea striata*, the bark of which is said to contain 17.84 per cent. tannin.

Belar (see Bull oak, p. 16).

Birch Bark (White birch) (*Betula alba*).

The inner bark of *B. alba* contains up to 6 per cent. of a catechol tannin. It is largely used in Russia in the production of light leathers.

Black Locust (False acacia) (*Robinia pseudoacacia*).

According to Möller, a German extract works produced extract from this material in 1918. The tannin content of the bark and wood varies of course with age, but the following figures are given :—

	Bark.		Wood.	
	Young.	Old.	Young.	Old.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Tannin	2.2	7.2	4.0	3.4
Soluble non-tannins	6.4	4.5	2.2	2.1
Insoluble matter	59.0	78.3	56.9	80.6
Moisture	32.4	10.0	36.9	13.9
	100.0	100.0	100.0	100.0

The tannin present in the bark is of the catechol group, and that in the heartwood a mixture of catechol and pyrogallol tannins. The prepared liquid extract shows :—

	Per Cent.
Tannin	25.1-25.6
Soluble non-tannins	12.0-14.1
Insoluble matter	2.2-2.8
Moisture	58.5-60.1
Specific gravity	22.8° Bé.-23.6° Bé.

Blue Fig Bark (Quadong) (*Elæocarpus grandis*).

This Australian bark (New South Wales) contains 10.28 per cent. of tannin, according to Maiden.

Box Myrtle (in China, yangmoe) (*Myrica nagi*, Thumb.).

The bark of this evergreen tree found in the Malay Islands and Japan is occasionally used for tanning. Perkin and Hummel give its tannin content as 27.3 per cent. It also contains the colouring matter myricetin, $C_{15}H_{10}O_8$.

Bull Oak, Belar (*Casurina glauca*).

Maiden gives 11.58 per cent. as the tannin content of this New South Wales bark.

C

Cabbage Palmetto (see Palmetto, p. 70).

Camanchile Bark.

In a review of the tanning industry of the Philippines, Gana says that this bark is one of the most favoured tanning materials on account of the light colour of the leather produced. An analysis of the dried bark gave :—

	Per Cent.
Tannin	25.36
Soluble non-tannins	9.41
Insoluble matter	65.23
Moisture	...
	100.00

The tannin is of the catechol class.

Canaigre (from cah-na-ger, meaning saw cane) (*Rumex hymenosepalus*).

The roots of this plant, sometimes known as "red dock," "wild rhubarb," and "tanners' dock," are used by Mexican tanners, while it has been introduced into British tanneries, although, for some years now, very little has been heard of the material. It has also been grown in Queensland.

The tannin content of the dry roots varies from 18-43 per cent. (catechol), although 30 per cent. is said to be the average for the Australian product. In the green state the tannin content is 9 per cent. with 70 per cent. water. Two early analyses by Schroeder gave :—

	Per Cent.	Per Cent.
Tannin	34.91	27.72
Soluble non-tannins	18.14	9.40
Insoluble matter	35.95	48.19
Moisture	11.00	14.69
	100.00	100.00

Norton, in writing on canaigre as found in Mexico, states that young roots contain 10 per cent. of tannin, which increases

to 28 per cent. when the plant attains an age of about three years. His figures for air-dried roots are :—

	Per Cent.
Tannin	27.8-34.9
Non-tannins	9.4-18.1
Insoluble matter	33.9
Carbohydrates	6.8
Ash	1.9-2.1

The tannin is readily soluble in water, and penetrates hide fibre quickly.

As with other materials, extract has been manufactured from the roots, the average composition of which is :—

	Per Cent.
Tannin	50
Soluble non-tannins	28
Insoluble matter	2
Moisture	20
	100
Sugars	12

A characteristic constituent of canaigre is starch, the presence of which is stated to give a little trouble during leaching, and in this connection extraction should be done at a fairly low temperature, 40°-50° C.

As might be expected from the large quantity of sugar present, liquors prepared from canaigre rapidly develop acidity. It gives a soft leather of a fairly light colour, and serves as a gambier substitute.

Caparrosa (*Ludwigia caparrosa*, Baill.).

The bark from this tree grown in Brazil contains from 20-25 per cent. of tannin.

Cape Sumach (*Osyris compressa*), *Colpoon compressum*.

The ground leaves marketed as Cape Sumach must not be confused with true sumach (*Rhus coriaria*) with which it differs both in tanning qualities and tannin content.

Some analyses of typical samples are given below :—

Tannin.	Soluble Non-Tannins.	Insoluble.	Moisture.	
Per Cent.	Per Cent.	Per Cent.	Per Cent.	
12.9	14.6	61.3	11.2	Imp. Inst.
13.6	21.4	53.8	11.2	"
19.94	28.27	40.60	11.19	"

Two samples of leaves from *Osyris abyssinica* or "Watta" leaves have been examined at the Imperial Institute and shown to contain about 24 per cent. tannin and 11-13 per cent. of non-tannin matter. These samples were obtained from Somaliland.

Cascalote (*Cæsalpinia cacolaca*).

The pods of this tree are similar to those known as divi-divi (*C. coraria*), and are used largely by the natives of several Mexican cities for tanning by a process similar to the English "bottle" method of sheepskin tanning. The pods contain about 40 per cent. of tannin, but only a very small quantity has found its way to England, as the total exports from Mexico are unimportant. The material gives a liquor prone to rapid fermentation, and, like divi-divi, produces a very light coloured leather when used alone.

Catechu (see Cutch, p. 21).

Cedar (Japanese) (*Cryptomeria japonica*, Don.).

The bark of this tree contains 6.3 per cent. of tannin, but is not used to any extent for tanning.

Cevalina (Bogata divi-divi) (*Cæsalpinia tinctoria*, Berth).

The pods from this tree have similar tanning properties to guara and divi-divi, and contain a pyrogallol tannin.

An analysis by Bennett shows the following composition :—

	Per Cent.
Tannin	31.9
Soluble non-tannins	19.2
Insoluble matter	43.1
Moisture	5.8
	100.0

Colour of 0.5 per cent. tannin solution—

Yellow	0.8 units
Red	1.6 "

The above writer considers cevalina to be a useful material for the production of light leathers, but not for use as a substitute for sumach in the bleaching of leathers as no reducing substances are present.

Chestnut (*Castanea vesca*, Gaertn.) (*Castanea vulgaris*, Lam.).

The wood of this tree, so largely grown in France, forms the raw material for the manufacture of chestnut extract.

According to Paessler, the wood may be used for this purpose when taken from trees of twelve to eighteen years old, when the tannin content will range up to 11 per cent. (pyrogallol). Decomposed wood is never used in extract making, as, in addition to giving an excessively dark extract, the tannin content of such wood is very small, and as much as 50-60 per cent. is lost through decomposition. Chestnut extract, as met with in commerce, has a sp. gr. of 1.20-1.23, the tannin content of French extract ranging from 26-30 per cent. Dry American chestnut powder is largely used in America, while importations into this country of both materials are considerable. As a rule, it is found that the colour (½ per cent. tan solution) of the American product is darker than the French makes, due in the main to the methods of manufacture. Extraction of the chipped wood is made either in open vats of wood or copper, or under pressure in autoclaves, and although many factories use the latter process, the open vat system is considered to be the better of the two. Under pressure, more non-tannin substances are extracted and a certain loss of tannin occurs; thus, although the total yield of extract is greater, the quality is inferior to that made by open vat extraction. To illustrate the influence of pressure extraction, some figures by Paessler will be quoted:—

Pressure in atmospheres	1	3	3	4	5	7
Duration in hours	...	1	2	1	1	1
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Tannin	11.2	11.2	10.7	10.9	9.6	7.6
Non tannins	3.4	4.3	5.9	7.1	11.5	17.1
Glucose	0.4	0.6	1.0	1.4	2.5	5.7
Cane sugar	0.3	0.5	1.0	1.5	3.4	5.7

The bark also contains tannin, and it has lately been suggested by Paessler that it could well substitute oak bark with which it is similar. A sample from Alsace gave:—

	Per Cent.
Tannin	9.7
Soluble non-tannins	8.3
Insoluble matter	67.5
Moisture	14.5
	100.0
Total sugars	4.8
Glucose	4.3

An interesting fact also on record is that the prickly husk of the chestnut contains 10-13 per cent. of tannin with 3-16 per cent. of non-tannins, while the brown husk shows 7-9 per cent. of tannin and 5-8 per cent. of non-tannins.

Coast Honeysuckle (*Banksia intergrifolia*).

A New South Wales sample of bark showed 10.82 per cent. tannin.

Cu-Nao (*Dio scorea alropurpurea*, Roseb.).

A so-called extract is prepared from the tubers of this plant by slicing and drying. A sample of this product from Indo-China examined by Jalade gave the following figures:—

	Per Cent.
Moisture	16.43
Tannin	20.20
Soluble non-tannins	7.07
Insoluble matter	56.30
	100.00
Starch	26.8
Proteins	3.24
Fat	0.32
Cellulose	25.94

The tannin belongs to the catechol group. It is understood that the material is also known by the name of Chinese gambier.

Cutch (Catechu) (*Acacia catechu*, Willd.).

True cutch is the extract prepared from *A. catechu*, although the same word is frequently used to describe mangrove extract, *i.e.*, mangrove cutch. The tree is grown largely in India and Burma, and in the better grade of extract only the heartwood is used. The solid extract contains from 58-60 per cent. of tannin, but is rarely used in the leather trade for tanning. It is a dark coloured material, and has a number of serious defects. It finds large application in the textile trade for dyeing and mordanting. (It can also be used for mordanting chrome leather.) Cutch is extensively used for "tanning" fishing nets and sails, and in this direction no other material has been found to give the same beneficial results. It lengthens the life of the sails and nets, and makes them more resistant to the action of sea water.

D

Deep Yellow Wood (*Rhus rhodanthema*).

The bark of this New South Wales tree has been found to contain 23.15 per cent. of tannin, and the dry leaves 16.91 per cent.

Dhawa (*Anoglissus latifolia*).

The leaves of this tree are used in India under the name of country sumach, and according to Pilgrim contain a pyrogallol tannin. The prepared "sumach" contains from 25-40 per cent. of tannin calculated on the dry material.

Divi-Divi (*Cæsalpinea coriaria*, Willd.).

The pods of this tree, found in the West Indies, Brazil, and part of Central America, contain a high proportion of a pyrogallol tannin. A typical analysis quoted by Norton is as follows:—

	Per Cent.
Moisture	13.5
Tannin	41.5
Soluble non-tannins	18.0
Insoluble matter	25.4
Ash	1.6
	100.0
Carbohydrates	8.4

The carbohydrates mentioned are undoubtedly all sugars, and this accounts for the rapid fermentation which takes place when an infusion of divi is allowed to stand for even a short space of time or during severe thunderstorms, when a red colouring matter is deposited. This fermentation may be partly prevented, by the use of a small amount of an antiseptic such as phenol (carbolic acid), and in the manufacture of divi-divi extract, the addition of such antiseptics as formic acid or mercuric iodide is suggested by Noyer and Dumesny.

Divi-divi has also been grown in India, and Fraymouth and Pilgrim quote 44.52 per cent. tannin and 23.57 per cent. soluble non-tannins on the perfectly dry sample. Here again it will be noted, as in other instances of tanning materials from India, that the proportion of non-tannins to tans is comparatively high.

The tannin of divi-divi is easily extracted from the

pods by means of hot water, but leaching with boiling water should not be done, as, under these conditions, decomposition and thus loss of tannin will take place. The colour of leather tanning by divi alone is of a nice light yellowish tint, but is inclined to be soft and spongy. Hence it is generally used in conjunction with other more astringent materials. It has been suggested as a successful substitute for gambier and valonia.

In addition to the tanning industry, this substance finds application in the textile trade as a mordanting agent.

Douglas Fir (*Pseudotsuga mucronata*, Raf.-Sudworth).

This tree, also known on the Pacific Coast as bregon pine, has been examined as to its suitability for tanning purposes by Benson and Thompson, whose results are summarised in the following table:—

	Sawmill Bark.	Sawmill Slab.	Fresh Bark.	Cambium Layer.	Sawdust.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Tannin	6.34	5.92	2.62	9.92	1.06
Soluble non-tannins	7.02	7.10	6.74	9.36	3.34
Insoluble matter	77.58	80.07	76.37	60.13	80.09
Moisture	9.06	6.91	14.27	20.59	15.51
	100.00	100.00	100.00	100.00	100.00

Dragon's Blood (*Pterocarpus draco*, Linn.).

This tree, which attains a height up to 30 ft., grows in Jamaica. In order to obtain the red sap, which when dried is known as dragon's blood, incisions are made in the bark. An early analysis gave the following figures:—

	Per Cent.
Tannin	34.85
Moisture	25.40
Ash	2.36
Insoluble matter	4.05
Gummy matter	33.34
	100.00

This material is not used for tanning, but on account of its deep red colour is used for dyeing horn, marble, etc., and finds many applications in the drug trade.

E

Eland's Boontjes (*Elephantorrhiza Burchellii*).

The only published accounts of the composition of the roots of this plant appeared in the Bulletin of the Imperial Institute, and later in the *South African Journal of Industries*.

The shrub grows well all over South Africa, and the roots were used by the Boers for tanning purposes.

The composition of the root is as follows:—

	Analyses by C. Williams.			Imperial Institute.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Tannin	7.4	6.2	17.1	19.6
Soluble non-tannins	8.2	5.8	23.3	20.0
Insoluble matter	13.7	12.3	49.7	48.4
Moisture	70.7	75.7	9.9	12.0
	100.0	100.0	100.0	100.0
Ash	..	...	...	2.7
Sugars as dextrose	...	...	...	16.8

It produces a soft but tough leather of a pale pinkish-brown colour. It is stated by Williams that it would not serve well as an extract-making material, owing to the large amount of sugar present, which would, in the prepared extract, be very liable to fermentation.

Emu Bush (*Eremophila longifolia*).

A sample from New South Wales gave:—

Bark	5.1 per cent. tannin	
Leaves	9.7 „	„

Eucalyptus Species (Various).

See also Kino (p. 40) and Mallet (p. 42).

The composition of some little-known eucalyptus species

are given below, the figures being by Maiden of New South Wales plants :—

Botanical Name.	Local Name.	Bark Tannin.	Dry Leaves.
		Per Cent.	Per Cent.
E. stellulata - -	Black gum or black sally	12.86	16.62
E. sieberiana - -	Cabbage gum	36.96	2.39
E. siderophloia	Red iron bark	10.4	5.95
E. amygdalina -	Ribbon gum	...	1.81
E. piperita - -	Messmate	...	[illegible].59
E. viminalis - -	Manna gum	7.5	4.0
E. Stuartiana - -	Apple tree	5.25	10.16
E. corymbosa -	Bloodwood	5.85	18.37
E. maculata - -	Spotted gum	9.74	5.26
E. Gunnii - -	Red gum	11.35	16.50
E. robusta - -	Mahogany	...	12.07
E. odorata - -	White box	...	6.77
E. obliqua - -	Stringy bark	17.2	...

F

False Acacias (see Black locust, p. 16).

G

Gall-Nuts.

Gall-nuts are formed as the result of the punctures of certain insects (Cynips) on the leaves, etc., of oak trees. They are mainly obtained from the oaks growing in Levant, Smyrna, etc., and find application mainly in the textile trade as a mordant and for the manufacture of inks.

Levant galls contain about 77 per cent., according to early figures, but this appears an extraordinarily high quantity, and it is probably lower than this. Aleppo galls contain from 60-66 per cent., while the Smyrna variety runs to about 60 per cent. Galls from *Pistacia vera* from India gave, according to Blockey, 30.1 per cent. tannin, 17.8 per cent. non-tannins, and 9.7 per cent. moisture. Chinese galls are formed by the punctures of another type of insect on a variety of sumach, and a sample examined at the Imperial Institute was reported upon as follows (Abst. *Leather World*, 1913, p. 554):—

These gall-nuts were said to have been produced on *Rhus semialata*, Murr., and are known to the Chinese as "Ng pui tze."

The sample consisted of brown, hollow galls, composed of a horny, translucent material, and containing a greyish-white granular powder, which emitted an unpleasant odour when the galls were broken. They were examined with the following results:—

	Per Cent.
Moisture	11.7
Ash	2.0
Tannin	61.5
Matter soluble in water (non-tannin)	7.1

The colour of a solution containing 0.5 per cent. of tannin, examined in a 1 cm. cell, was 0.4 red; 0.7 yellow.

The galls were submitted to a firm of commercial experts, who reported that they were of good, marketable quality, and valued them at from £55 to £60 per ton, ex-ship, London (June 1912). This price compared very satisfactorily with that of ordinary Chinese galls, which on the same date were quoted at from £49 to £52. 10s. per ton in London.

The galls from *Tamarix articulata* have been found to contain 55.8 per cent. of tannin and 10.9 per cent. of non-tannins.

Incidentally, Chinese galls form the raw material for the preparation of pure tannic acid. The method used is outlined

by Perkin and Everest in their work on "Natural Organic Colouring Matters."

The crushed galls are treated with water at 50°-60° C. to form a concentrated solution, and then filtered. The clear solution is then treated with one-fourth of its volume of ether, and the emulsion allowed to separate. The watery liquor is run off, freed from ether in solution, and the syrup dried off over a steam coil on tin plates. Any wax, etc., present is removed by washing with ether, or the solution of the material precipitated with common salt solution, and then redissolved in ethyl acetate. This latter solution is then evaporated under reduced pressure.

"Gallol" Root Bark (*Acacia*, Sp.).

This is a light coloured bark, which when used for tanning gives a pale pink coloured leather. A sample from Somaliland, examined at the Imperial Institute, gave:—

	Per Cent.
Tannin	24.0
Soluble non-tannins	7.7
Moisture	12.0
Insoluble matter	56.3
	100.0
Mineral ash	4.6

Gambier (Terra japonica, yellow cutch) (*Uncaria gambier*).

Up to quite recent times commercial gambier was prepared in a very crude manner by native labour chiefly in Borneo. An authentic description of the methods used has been described by Hough (*Collegium*, London, 1915, p. 343). The trees grow to a height of about 10 ft., and the small twigs and leaves from which the extract is made are removed by a curiously designed cutter known as a "pisan dammar." The twigs are next prepared for extraction by chopping into 5-in. lengths, when the material is put into an iron pan and boiled with two successive quantities of water. The last liquor is further used for the first extraction of a fresh lot of material. During boiling, frothing and loss due to boiling over is prevented by having a bottomless wood vat cemented to the rim of the iron pan and by suspending in the liquor an arrangement of concentric circles of rattan fixed to a bamboo pole.

When the boiling is considered to have been carried far enough, the liquor is strained free from solid particles, thickened by the addition of rice meal, and the whole allowed to set in boxes lined with sacking and having perforated bases. Excess of water (and some tannin consequently) is allowed to run off and the sides of the boxes removed so as to obtain a block of gambier paste. The paste is cut into small cubes by means of string, and dried off in the sun and finally finished off on the roof of the factory.

Analyses quoted by Hough of Borneo gambier are given below:—

	Gambier Leaf.	Same Extracted.	Cube Gambier.
	Per Cent.	Per Cent.	Per Cent.
Tannin - - -	5.5	2.6	35.0
Soluble non tannins -	3.3	2.5	31.0
Insoluble matter -	29.2	32.9	21.9
Water - - -	62.0	62.0	12.1
	100.0	100.0	100.0

Hence it will be seen from the two first analyses that only about 50 per cent. of the total tannin in the leaves is extracted by this native process. The tannin belongs to the catechol group. At the present time a make of gambier known as "plantation" or "Asahan" is put on to the market, and is manufactured under more ideal conditions than the ordinary cube variety. Copper extractors are used, and the liquor, after careful clarification, is evaporated in vacuum evaporators.

An analysis of Asahan gambier by Paessler gives:—

	Per Cent.
Tannin - - - - - -	37.0
Soluble non-tannins - - -	28.2
Insoluble matter - - - -	4.3
Moisture - - - - -	30.5
	100.0

A great difference is the low amount of insoluble matter, which is a distinct advantage and is due to careful preparation, the absence of vegetable debris and rice meal.

In commerce it is the custom to sell Asahan gambier with a maximum moisture content of 31 per cent. Indragiri

Plantation gambier (made in Dutch East Indies) is also sold on a maximum moisture guarantee of 31 per cent., and how close this standard is adhered to may be gathered from the following analyses of this make by Paessler (*Gerber Zeitung*, 1908):—

	Per Cent.	Per Cent.	Per Cent.
Tanning matters	37.6	37.1	38.9
Soluble non-tannins	30.4	29.3	24.2
Insoluble	0.8	3.3	4.2
Water	31.2	30.3	32.7
	100 0	100.0	100.0

Some further analyses of commercial cube gambier published by Brumwell (*J.S.C.I.*, 1911; *Leather World*, 1911, p. 554), are given below for reference:—

	Cube Gambier.			Block Gambier.		
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent
Tanning matter	42.3	48.8	42.6	39.2	36.3	34.6
Soluble non-tannins	31.8	32.3	32.9	31.9	26.2	24.7
Insoluble	11.2	9.3	9.8	15.1	10.1	11.0
Water	14.7	13.6	14.7	13.8	27.4	29.7
	100.0	100.0	100.0	100.0	100.0	100 0
Ash	5.4	4.2	3.7	4.3	4.4	4.5
Tintometer readings—						
Red	...	1.6	1.9	2.5	...	2.4
Yellow	...	4.8	4.7	5 1	...	5.9

The tannin of gambier belongs to the catechol group.

As a tanning material, gambier is characterised by giving a soft leather and is used in admixture with more astringent materials for the tanning of both heavy and light leather. In addition it is a favourite material for the dressing of fur rugs when it is used in conjunction with alum and salt.

Gothar (Gottahar, Gotti, Gotbhor, Ghont) (*Zizyphus xylopyrus*).

The fruit of this Indian tree is said by Guthrie, in his report on the leather industries of Bombay, to yield a very good leather when used by the natives. It contains a fair

proportion of mucilaginous substance which renders extraction somewhat difficult. Recent tests by Pilgrim and Fraymouth show the following results: Tannin, 21.17 per cent.; non-tannins, 25.91 per cent.; insolubles, 52.92 per cent.; water, nil. These figures apply to the dry fruit after extraction of the stones, these latter containing only 3.9 per cent. of tannin calculated on the dry matter.

Guara (*Paullinia sorbilis*).

According to Norton this small tree is found in Brazil, and the pods contain 55 per cent. of tannin. Recent analyses by Callan (*J.S.C.I.*, 1915, 645) hardly bear out this high percentage of tannin. These are given herewith :—

Tannin.	Non-Tannins.	Insoluble.	Moisture.
Per Cent.	Per Cent.	Per Cent.	Per Cent.
43.5	23.8	22.0	10.7
46.2	25.8	19.0	9.0
48.4	23.2	17.7	10.7
44.8	23.1	21.7	10.4

Attempts to prepare a satisfactory extract from this material do not appear to have met with much success, as a sample examined by Callan showed a lower percentage of tannin than the raw material :—

	Per Cent.
Tannin - - - - -	41.7
Soluble non-tannins - - -	30.0
Insoluble matter - - - -	11.0
Moisture - - - - -	17.3
	100.0

It would appear to the present writer that there seems very little purpose in making an extract from such a rich tanning material.

The tannin is of the pyrogallol class and resembles that in myrobalams. As is usual with these fruit or pod tannins, guara gives a soft leather similar to gambier tanned hide.

Guyacan (Guaycan, Quajacan) (*Cæsalpinia melanocarpa*, Griseb.).

The pods of this Argentine tree have been examined at the American Research Laboratory by Terrasse and

Anthes, who say that it resembles divi-divi with the exceptions that both tannin content and purity of the extract is lower. It has the following composition :—

	Per Cent.
Moisture - - - - -	11.40
Tannin - - - - -	22.53
Soluble non-tannins - - -	37.21
Insoluble matter - - - -	28.86
	100.00

The tannin of the pods belongs to the pyrogallol class giving a blue-black coloration with iron alum, and a negative reaction with bromine water.

Analyses by Levi and Sigel are :—

	Wood.	Pods.
	Per Cent.	Per Cent.
Soluble solids - -	9.08	34.68
Non-tannin -	0.99	19.90
Tannin - - -	8.09	14.78

H

Hemlock (*Tsuga canadensis*, Carr).

The extract of hemlock bark, commercially known as "hemlock" extract, is made from the bark of the American hemlock tree (*Tsuga canadensis*). This is a large tree found in the eastern highlands of North America, from North Carolina to Nova Scotia, the lumber from which came largely into use for building purposes after the white pine forests had been depleted. The bark from this tree formed the tanning agent of the characteristic American "red" leather of the nineteenth century. Prior to the time when hemlock lumber became valuable as a building material, many hemlock trees in the States of New York and Pennsylvania were cut down solely for their bark, the stripped trunk of the tree being allowed to rot where it fell.

The trees are cut down in the spring of the year, and the bark immediately peeled, or stripped off, and allowed to lie flesh side up until the film of sap is dried, after which the bark is put up in small piles to await removal from the woods to the tannery.

The tannin content of the bark varies with the locality in which the tree grows, and will run from 7-12 per cent. (catechol group).

The hemlock bark of Pennsylvania and of the Michigan peninsula is generally regarded as the richest in tannin. The hemlock of Wisconsin, Virginia, and North Carolina does not contain as much tannin as the Pennsylvania and Michigan bark.

The process of making hemlock extract follows closely the old methods of extracting the tannin in making up the liquors for the tannery. To these methods is added a concentration process for converting the extracted liquor into extract of varying degrees of concentration, ranging from 25° Bé. to the solid or dry powder form.

For best results in leaching, the bark should be dry, and the bark is accordingly allowed to remain in the stack, or pile, for at least six months after being peeled from the tree. The dried bark is prepared for the leaching process by means of a bark mill, or shaver, consisting of a revolving segmented disc, having knives set in the periphery and actuated by a vertical shaft; the ground

bark is handled by a fan and separator, the latter removing the dust, while the blast of air carries the balance of the ground bark to the leach house. Shredders, or pulverising machines, are not used in grinding hemlock bark, as that class of machine produces a preparation containing too much fine bark, which serves to interfere with proper circulation of the leaching liquor.

After the grinding preparation, the bark is ready for leaching, by either the open vat method with atmospheric pressure, or by the closed or autoclave method, involving higher pressures and temperatures. Almost all of the American hemlock extract is made by open vat extraction. One or two factories use pressure extraction in autoclaves, but on account of the nature of the bark, there are mechanical difficulties encountered in emptying the autoclaves after the pressure extraction has been completed. To overcome this difficulty a little chestnut wood is sometimes mixed with the bark when the autoclave is filled; the wood serves to keep the bark from packing too tightly, and the leached residue is more easily expelled from the autoclave. The percentage of wood used for this purpose is not large, but, of course, serves to prevent the product being classified as absolutely pure hemlock extract.

The open leach vats used in practically all of the hemlock extract factories are the same as used in the tannery leach houses, and are made of pine, cedar, or cypress, preferably of a diameter greater than their height, as too high a column of the ground bark interferes with circulation. The leaches are arranged in sections of six or eight, hot water being put on the "tail" leach or end vat, and the liquor travelling successively from the "tail" to the "head" leach, gaining strength as it passes through the different leaches, until it reaches the "head" leach which contains the freshly ground bark. The liquor coming from the preceding leaches in the section is at this stage pumped to a box located on the top of the leach, and from this box passes to a detachable revolving sprinkler which distributes the liquor evenly over the top of the fresh bark. The warm liquor percolates through the bark, and when the mass is saturated and the head leach filled with liquor, which has now attained its maximum specific gravity, the strong liquor is taken to the storage tanks preparatory to concentration.

Different methods of handling the liquors in the leach house are in vogue. Some factories use a percolation method,

by which the liquor flows by gravity from the tail leach successively through the other leaches in the section until it reaches the head leach; the bark by this method is continuously under liquor. The liquor flows on the top of the leach, passes down through the bark column, out through a pipe leading from the bottom of that leach to the top of the next leach in the section, and thus flows to the top of bark column in the next leach, and the flow continues until the head leach is reached. Frequently, this gravity flow is aided by air lift pumps operating in the pipes leading from the bottom of one leach to the top of the next leach in the section.

At other factories a "decoction" system is in effect by which the liquor is pumped from leach to leach, either by air or by mechanical pumps. In this system the liquor is allowed to stand idle in the leaches for a certain length of time, during which "decoction" takes place, and the entire volume of liquor is then pumped to the next leach ahead, this latter leach having previously been emptied of liquor in the usual course of operating by this system.

Whether the percolation or "decoction" system is used, the liquor going on the fresh ground bark in the head leach is generally applied by the revolving sprinkler, as this serves to wet the bark evenly, and prevent "channelling" and "floating," which would take place if the liquor was put on at one point or too rapidly.

The moving liquor is heated either by coils or direct steam in the leaches, or in the "decoction" system by steam coil liquor heaters through which the liquor is pumped when it is passed from one leach to the next. The leaches are provided with slatted false bottoms to prevent particles of bark clogging the liquor lines. Steam coils are sometimes placed on the bottom of the leaches, between the true bottom and the false bottom. In some systems coils of steam pipe, or direct steam lines, are placed directly in the liquor lines leading from the bottom of one leach to the top of the next leach. Water near the boiling point is put on the tail leach of practically spent bark, and the liquor on the last two or three leaches in the section is maintained at a temperature close to 200° F. The temperature lowers as the head leach of fresh bark is reached, so that the liquor going on the fresh bark is generally between 140° and 150° F.

At the end of the cycle of the leaching process the tail leach of spent bark is drained by gravity, or by pumps, and the bark removed by hand or by mechanical leach casters,

and conveyed to the boiler room where it is burned with coal in Dutch ovens to provide heat for the boilers.

The liquor from the leach house is pumped to the storage tubs, from which it is piped to the multiple effect copper evaporators which concentrate it to the desired strength. The liquid extract is generally made up to approximately 25 per cent., or 27 per cent. tannin strength, and is shipped in tank cars for domestic use and in hardwood casks for export trade.

A clarified extract is sometimes called for, and this is generally made by the use of sodium bisulphite (see also p. 132). The solid sodium bisulphite is frequently used in the leach house, the desired amount being added to the fresh bark in the head leach. When the clarification is applied to the liquor, the chemical is added to the warm liquor in the storage tubs. A crude clarification is accomplished by adding the bisulphite to the hot extract as it comes from the vacuum pan, and thoroughly stirring the resulting mixture.

The dry powder form of hemlock extract contains from 54-58 per cent. of a catechol tannin, and is made from the finished liquid extract. The dryer consists of a steam-heated, hollow bronze cylinder which revolves in an outer metal casing in which a vacuum of about 27 in. is maintained (see also p. 146). At one point in its revolution the cylinder dips into a tray of the liquid extract and is coated with a film of extract. This film becomes dry before a revolution of the cylinder is completed, and the dried film of extract is scraped off by a knife, falls into a conveyer which carries it to receivers from which it is removed and packed in bags. The cylinder makes from seven to nine revolutions per minute, so that the extract is in contact with the heat for only a few seconds, and as the operation is carried on under a high vacuum, there is no effect on either colour of the extract or on its solubility. For firmness and weight-giving properties, hemlock is said to be one of the best materials, but, owing to the absence of any appreciable amount of sugars, hemlock liquors do not produce acids by fermentation. It is usual to add a little organic acid, although in America it is believed that sulphuric acid is used for this purpose. From the standpoint of English tanners, hemlock may give a too dark coloured leather, but used in conjunction with other materials, this drawback may, to a very large extent, be overcome.

Hemlock Spruce, Indian (*Abies dumosa*, Loudon).

Trimble's analysis shows tannin 10.26 per cent., with a moisture content of 12.24 per cent.

Hemlock, Western (*Tsuga heterophylla*, Raf.-Sargent).

Benson and Thompson say that this bark has been used at least in one Washington tannery in the manufacture of skirting leather for saddles. The composition of the bark is as follows (calculated on dry bark):—

	Washington.	Pennsylvania.	Quebec.
	Per Cent.	Per Cent.	Per Cent.
Tannin	17.04	13.28	10.16
Soluble non-tannins	6.40	7.52	4.56
Insoluble matter	76.56	79.20	85.28
	100.00	100.00	100.00

Indian Materials (Various).

The following analyses (on dry materials) of various Indian tanstuffs have been compiled from the "Esociet Research Bulletin," No. 1, by Fraymouth and Pilgrim:—

Botanical Name.	Tanin.	Non-Tannins.	Insoluble.	Common Name.
	Per Cent.	Per Cent.	Per Cent.	
Michelia excelsa - -	6.57	12.28	81.15	...
Tamarix dioica (bark) -	10.16	9.98	79.86	Jhao
Heritiera fomes (bark) -	7.34	4.36	88.30	Sundri bark
Zizyphus nummularia (bark)	9.89	12.73	77.38	Ber
Acer Campbellii (bark) -	3.19	6.84	89.97	Himalayan maple
Anacardium occidentale (bark)	9.43	9.40	81.17	Kashew nut tree
Bauhinia vahlii (bark) -	9.29	14.55	76.16	Muhurain bark
B. racemosa - - -	2.30	...	...	...
Bucklandia populanea -	10.67	10.03	79.30	...
Anogeissus acuminata (bark)	10.06	8.74	81.20	Yon
A. pendula (bark) -	9.09	6.60	84.31	...

This by no means exhausts the number of possible tanning materials available in India, and the reader should consult the original "Bulletin" for further analyses.

As will be seen from above, and elsewhere in this book, India is the source of a number of valuable tanning materials, and it remains only to put the matter on a working basis under skilled supervision. The writer is informed by Mr Fraymouth that such is being done at the present time, and expectations are high at the possibility of India becoming a valuable extract producing country. He himself has carried out extensive researches on the subject, the results of which are of far-reaching importance. Apart from materials already mentioned, there is available a leaf product, which, when dried and ground, contains 48-50 per cent. of tannin, and has the property of bleaching reds, and would therefore serve as an

admirable bleaching agent. The available amounts of the chief tanstuffs are very considerable, and Mr Fraymouth informs the author that when the necessary organisation has been established, at least 20,000 tons of each would be available. It is considered that no tanstuff should be taken the collection of which entails the destruction of the tree, and the truth of this statement will be fully appreciated by those conversant with Indian tanning materials.

Iron Wood (*Hopea parviflora*).

Pilgrim states that the bark known by this name is a by-product from the timber trade in India and has the following composition:—

	Young Bark.	Old Bark.
	Per Cent.	Per Cent.
Tannin	17.06	21.71
Soluble non-tannins	4.60	4.69
Insoluble	78.34	73.60
Moisture	0.00	0.00
	100.00	100.00

J

Jamba Bark (*Xylia dolabrifomis*).

This bark, although containing a fairly high proportion of tannin, is stated by Guthrie to be seldom used in the tanning industry of India (Bombay). It finds application in the "tanning" of fishing nets.

An analysis by the above chemist gave:—

	Per Cent.
Tannin	18.5
Soluble non-tannins	5.1
Insoluble	69.7
Moisture	6.7
	100.0

Juniper (Weeping blue, of Japan) (*Juniperus recuva*, Ham.).

In an article on Japanese cedars and other trees, Trimble states that a sample of this bark gave 8.32 per cent. tannin on the air-dried material.

K

Khaki (? *Diospyros khaki*).

The composition of the extract prepared and sold as khaki extract is given by Jalade ("Le Cuir," 1920, p. 94) as follows:—

	Per Cent.
Tannin	57.00
Non-tannins	22.00
Insolubles	0.70
Moisture	20.30
	100.00

The tannin belongs to the catechol group, and only mere traces of reducing sugars are present.

"Kili" Bark (*Fiscus*, Sp.).

This bark, from the Sudan, has been analysed at the Imperial Institute, which gives the following composition:—

	Per Cent.
Tannin	18.95
Soluble non-tannins	4.25
Insoluble matter	65.83
Moisture	10.97
	100.00

It is stated, in addition, that it gives a harsh, deep reddish-brown coloured leather.

Kino.

Kino is the general name given to the gummy exudations found on the barks of certain trees. Although very rich in tannin, the kinos are not used for tanning, except, perhaps, in isolated cases. In the first place the quantity available is not at all large. Their chief application is in medicine. Some early analyses by Maiden of kinos from New South Wales trees are given below:—

	Tannin. Per Cent.
Eucalyptus maculata (spotted gum)	44.55
E. amygdalina (ribbon gum)	57.76
E. siderophlora (red iron bark)	35.18
E. corymbosa (bloodwood)	28.44
E. macrorrhyncha	54.12
E. piperita (messmate)	62.12

So far, the kinos have been found to contain catechol tannins.

Some later and more complete analyses are those by F. A. Blockey, *J.S.C.I.*, 1902, and are given below for reference:—

	Local Name.	From	Tannin.	Sol. Non-Tan.	Insol.	Water.
			Per Cent.	Per Cent.	Per Cent.	Per Cent.
Eucalyptus siderophlora	"Iron bark" kino	Cambevarra, N.S.W.	73.2	4.0	6.4	16.4
E. amygdalina	"Ribbon gum" kino	N.S.W.	64.8	7.2	10.9	17.1
E. piperita	Kino	"	31.5	5.6	46.0	16.9
E. corymbosa	"Bloodwood" kino	"	30.3	2.7	54.3	12.7
E. punctata	"Grey gum" kino	"	38.3	5.0	42.9	13.8
E. stilluta	Kino	"	31.6	9.4	42.9	16.1

A gum kino known as Malabar kino—the dried exudation from *Pterocarpus marsupium*—is stated by Hooper to have the following composition:—

	Per Cent.
Moisture	12.2-15.7
Tannin	70.0-82.4
Insoluble matter	0-5.1
Ash	1-2.3

One hundred c.c. of the fresh kino yields about 50 gm. of the dry gum.

L

Larch (*Pinus larix*).

The bark of the larch contains 10-12 per cent. of a catechol tannin, and is used in Scotland for tanning sheepskins. It produces a fair amount of acid in the liquors, owing to the presence of sugars which rapidly ferment.

M

Mallet Bark (*Eucalyptus occidentalis*).

This Australian tan bark is one of the richest barks available, and its rapid gain in popularity is shown by the fact that the value exported in 1905 was £154,087, as compared with £859 for 1903. The Germans were large buyers of the material for the manufacture of extract.

It gives a firm light brown coloured leather devoid of the pinkish tinge common to mimosa tanned skins.

Its composition is:—

	Per Cent.
Tannin	42.0
Soluble non-tannins	8.0
Insoluble matter	35.5
Moisture	14.5
	100.0

While another analysis by Paessler gave:—

	Per Cent.
Tannin	39.1
Soluble non-tannins	11.9
Insoluble matter	34.5
Moisture	14.5
	100.0
Glucose	1.4
Cane sugar	0.8

Dekker has experimented with a mallet bark which had the composition:—

	Per Cent.
Tannin	31.7
Insoluble matter	35.7
Moisture	13.4
Mineral matter	5.74
Nitrogenous matter	0.44
Carbohydrates	19.17
Pentosans	8.10

The tannin belongs to the catechol group.

Mangoustan Shells (*Garcinia mangostana*, L.).

The pericarps of the fruits of *G. mangostana* are used by the natives of Cochin China for tanning and dyeing purposes.

An examination of this material by Maheu and Matrod gave the following results:—

	Per Cent.
Tannin	13.61
Soluble non-tannins	14.59
Insoluble matter	57.93
Moisture	13.87
	100.00
Sugars	Nil

The tannin belongs to the catechol class, giving a precipitate with bromine water, complete precipitation with H.CHO and HCl, and a greenish-black precipitate with iron salts.

Dekker has stated that the material also contains a yellow crystalline colouring matter—Mangostin—the constitution of which has not been established.

Mangrove Bark.

The mangrove barks of commerce are obtained from a variety of species, among which may be mentioned:—

Rhizophora mucronata, Lam.
Brugiera gymnorrhiza, Lam.
Ceriops candolleana, Arn.
Xylocarpus, etc.

The trees grow near the seashore, and are to be found in such countries as Borneo, Australia, Philippine Islands, West Africa, and India.

Australian Mangroves.—Of the Australian barks, a good account in the *Leather World*, by Coombs and Alcock, is abstracted below:—

Of the various mangroves, Rhizophora is the most common at Cairns and Cooktown, and represents fully 75 per cent. of the trees which it would pay to strip. The appearance of the arched roots above the water is a good guide to distinguish this variety from Brugiera, which carries the same dark foliage and general appearance common to Rhizophora, and the two are usually united under the name of Black Mangrove, although the vernacular names differ considerably in the various districts and are very misleading to persons collecting specimens in Australia. Rhizophora appears to be more common on the water side of the mud and sand banks, and Brugiera appears to grow best where the banks begin to shelve off to higher and firmer ground. The two, however,

are to be found at the water's edge at low tide, and mingle together right back to the extreme edge of the water at high tide.

Ceriops is found in almost all the mangrove localities, but it is the least common of the three varieties, and the tree is much smaller and would not yield anything like the same amount of bark as Rhizophora or Brugiera.

There are several other mangroves growing on the Northern Australian coasts, ranging from small shrubs to large trees, but the latter are decidedly scarce in many districts. The variety Carapa is also found among Australian mangroves, but it is not plentiful in the above mangrove districts.

Stripping the bark from mangrove trees is rather difficult work. Mr Range, of Queensland, fells the tree with the aid of a saw, cutting the butt nearly through when it falls, and it is left hanging to the stump, clear of the mud and water. The stripper can then easily remove the bark with a hatchet. It is not possible to cut a ring around the base of the tree and then pull the bark off in a similar manner to that of stripping wattle trees. The bark breaks off in lumps, and comes away freely from the tree.

The ross on nine samples averages 22.6 of the bark of Rhizophora, and in the following analyses are included the whole of the ross, but when stripping for commercial requirements a large percentage would be broken away. When stripping the bark the authors came to the conclusion that the percentage of ross on the barks of Brugiera and Ceriops is somewhat higher, but there is no doubt, like that of Rhizophora, they vary to a considerable extent. The following table shows the percentage of ross on eleven samples:—

Ross on Bark of Rhizophora.						Brugiera.		Ceriops.	
No.	Per Cent.	No.	Per Cent.	No.	Per Cent.	No.	Per Cent.	No.	Per Cent.
1	19.7	4	28.3	7	21	10	37.5	11	28.8
2	19.6	5	26.4	8	19.72				
3	23.4	6	24.8	9	20.7				

The appended table shows in tannin value an appreciable difference between the results of bark with and without ross.

The average tannin value of ross works out at about 6 per cent., and as the ross equals about 20 per cent. of

bark, it will be plain to the observer that the removal of part or all of the ross will *greatly increase* the tannin value.

We have prepared a table, giving the amount of moisture in barks of Rhizophora at the time of stripping. It is not possible to dry the bark where the trees are stripped, and strippers and extract manufacturers will have to convey the green bark to be dried at a convenient centre in the various districts where the bark is obtained.

	Barks with Ross.			
	1	2	3	4
	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Tannin	29.46	33.95	38.62	36.54
Non-tannins	10.93	10.31	9.58	9.14
Insolubles	47.11	43.24	39.3	41.82
Water	12.5	12.5	12.5	12.5
	100.00	100.00	100.00	100.00

	Barks without Ross.			
	1	2	3	4
	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Tannin	35.77	42.37	46.07	43.29
Non-tannins	13.10	12.24	11.14	10.71
Insolubles	38.63	32.89	30.29	33.5
Water	12.5	12.5	12.5	12.5
	100.00	100.00	100.00	100.00

	Ross.			
	1	2	3	4
	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Tannin	3.8	5.56	8.28	10.7
Non-tannins	2.12	2.59	3.24	3.11
Insolubles	81.58	75.35	75.98	73.69
Water	12.5	12.5	12.5	12.5
	100.00	96.00	100.00	100.00

The average yield of air-dried bark, containing 10.3 per cent. of water, taken from eleven samples of green bark, works out at 66.4 per cent., and the yield free from all water is 59.6 per cent. These samples were weighed immediately after stripping.

No.	Green Wet.	Air Dried.	Moisture.	Free from Moisture.
	Lbs.	Per Cent.	Per Cent.	Per Cent.
1	100	66.8	9.3	60.5
2	„	68.3	8.6	62.4
3	„	64.0	9.4	57.9
4	„	69.7	10.14	62.6
5	„	63.7	10.74	56.8
6	„	71.0	8.7	64.4
7	„	70.8	12.84	61.7
8	„	58.6	10.56	52.4
9	„	67.8	11.32	61.6
10	„	72.4	10.26	64.9
11	„	57.4	11.62	50.7
Aver.	100	66.4	10.31	59.6

The authors have dealt with the diameter of trees, which is not directly proportional to the age, but the cost of stripping is inversely proportional to the diameter of the tree, and the results obtained show that trees only 4 in. in diameter are suitable for stripping, and probably trees under 4 in., providing labour expenses are not too high.

Table showing Tannin Value compared with Diameter of Tree

Rhizophora

Diameter	4 in.	4½ in.	5 in.	6 in.	8 in.	9 in.	9 in.	9 in.	Moist
Tannin -	28.22	33.81	30.02	30.85	30.26	22.33	31.36	30.4	12.5
Diameter	10 in.	10 in.	10 in.	12 in.	15 in.	16 in.	16 in.	16 in.	...
Tannin	32.38	33.95	21.18	38.62	35.53	40.41	39.3	...	...

Above 12 in. diameter, 39.61, 35.76, 36.54

Brugiera

Diameter	5 in.	5 in.	7 in.	9 in.	9 in.	15 in.	19 in.	...
Tannin -	25.48	25.82	23.62	29.82	29.1	30.42	36.87	12.5

Ceriops

Diameter	4 in.	4 in.	5 in.	7 in.	10 in.	13 in.	...
Tannin -	25.78	30.96	30.51	31.85	32.43	32.02	...

From the above results it can be accepted as a general rule that the tannin value of the bark is highest in the largest trees, which usually carry the stoutest bark.

Of *Rhizophora mucronata*, it was found that the tannin value varies from 28-40 per cent., although two samples gave only 21.18 per cent. and 21.44 per cent., due to an abnormal growth of ross. This bark is not so stout as other samples, and, having more than an average proportion of ross, goes to prove conclusively that the inclusion of the ross has a material effect on the analytical results. The average of twenty-one analyses is as follows:—

	Per Cent.
Tannin	33.09
Soluble non-tannins	10.60
Insoluble matter	43.80
Moisture	12.50

The bark from *Brugiera gymnorrhiza* differs considerably from the barks of Rhizophora. The former is a coarse, open bark, which shows the fibres very plain when the bark is broken up for the mill; the latter is close, solid bark, which would always command a higher price if judged on appearance. Paessler (see later) finds that there is very little difference between the tannin value of Rhizophora and Brugiera, but our results agree with the difference described above, Brugiera, the more fibrous bark, containing the least tannin.

BRUGIERA GYMNORRHIZA (AUSTRALIAN)

No.	Tannin.	Non-Tannins.	Insolubles.	Water.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.
1	23.62	7.70	56.18	12.5
2	29.82	7.05	50.63	"
3	25.48	7.64	54.38	"
4	29.10	10.28	48.12	"
5	25.82	10.67	51.01	"
6	36.42	11.75	39.33	"
7	30.63	9.36	47.51	"
8	32.07	7.32	48.11	"
Aver.	29.12	8.97	49.41	12.5

Ceriops is well distributed throughout the mangrove districts of Australia, but the majority of the trees are too small for stripping, and the trees suitable are only a small percentage when they are compared with Rhizophora and Brugiera.

CERIOPS CANDOLLEANA (AUSTRALIAN)

No.	Tannin.	Non-Tannins.	Insolubles.	Water.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.
1	31.85	7.87	47.78	12.5
2	30.96	12.92	43.62	"
3	25.78	15.00	46.72	"
4	30.51	14.62	42.37	"
5	31.30	9.60	46.60	"
6	32.43	8.16	46.91	"
Aver.	30.47	11.36	45.66	12.5

Indian Mangroves.—As regards Indian mangroves, Fraymouth and Pilgrim in their very admirable report say that one of the most common varieties is *Ceriops candolleana* (*C. roxburghiana*), known locally as "Goran."

The composition of this bark together with other Indian samples are given below, the figures being summarised from the above report :—

INDIAN MANGROVE BARK

	Brugiera caryophylloides.	Ceriops roxburghiana.	Ceriops candolleana.	Rhizophora mucronata.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Tannin	18.41	27.73	22.60	22.17
Soluble non-tannins	10.49	8.15	10.72	16.76
Insoluble matter	71.10	64.12	66.68	61.07
Moisture	...	...	...	...
	100.00	100.00	100.00	100.00
Colour of ½ per cent. Tannin solution—				
Red	13.6	...	28	10.47
Yellow	30.21	...	43	26.85

It will be seen from the above figures, that Indian barks are poor in tannin content as compared with those from Australia, and this conclusion is also arrived at by the Imperial Institute after extensive tests of a number of barks.

East African Mangroves.—Paessler, in examining some bark from the late German East Africa, obtained the following results:—

	Lowest.	Highest.	Average.
	Per Cent.	Per Cent.	Per Cent.
Rhizophora mucronata, Lam.	29.3	40.8	36.5
Brugiera gymnorrhiza, Lam.	28.4	42.3	35.8
Ceriops candolleana, Arn.	24.2	32.3	25.8
Xylocarpus	26.7	32.5	29.8

It is consequently concluded that "on account of their high tannin content the Rhizophora, Brugiera, Ceriops, and Xylocarpus barks are worthy of consideration as tanning materials." At the same time investigations were made as to the influence of the time and manner of stripping the bark, and the results obtained are summarised in a series of tables. These show clearly that it is important to take into account the age of the tree, and also the particular part of the tree from which the bark is stripped. Generally the bark of the older trees contains the most tannin, although in some cases the opposite is to be observed. Usually also, but not always, the nearer the bark is to the ground the higher is its tannin content, and this applies to the bark from the branches as well as to that from the trunk of the tree. Barringtonia bark and the fruit from Xeretiara were also examined, but both contained so little tannin as to be out of the question for tanning purposes.

Mangroves from Various Sources.—A large number of samples of mangrove barks from different sources have been examined at the Imperial Institute, and the table on page 50 has been compiled from their published figures.

General Remarks on Mangroves.—The tannin of the mangrove barks belongs to the catechol class, and both the natural bark and prepared extracts are highly coloured. The earliest patent for the manufacture of mangrove extract was granted to J. Fisher (E.P. 5,311, 1883), who first washed out the salt with cold water, and then extracted the tannin under pressure.

Common Name.	Botanical Name.	Source		Tannin.	Non-Tannins.	Insoluble Matter.	Moisture.
				Per Cent.	Per Cent.	Per Cent.	Per Cent.
Red mangrove	Rhizophora mangle	British Honduras	...	20.2	11.0	56.2	11.6
,,	,, ,,	British Guiana	...	25.0	6.4	52.7	15.9
White mangrove	Laguncularia racemosa	British Honduras	...	12.3	6.0	69.7	12.0
Zaragoza mangrove	Conocarpus erectus	,,	...	18.7	3.6	61.7	16.0
Black mangrove	Avicennia nitida	,,	...	5.4	7.5	75.7	11.4
... ...	Pemphis acidula	Seychelles	Stem bark	42.54	9.36	36.04	12.06
... ...	,, ,,	,,	Scrapings from stem bark	19.98	3.75	63.82	12.45
... ...	Rhizophora mucronata	,,	Bark, old roots	33.90	12.50	42.68	10.92
... ...	,, ,,	,,	Bark, young roots	17.77	16.68	52.55	13.00
... ...	,, ,,	,,	Bark, old stems	35.04	9.00	44.50	11.46
... ...	,, ,,	,,	Bark, young stems	29.71	11.91	46.07	12.31
... ...	,, ,,	,,	Bark, old branches	34.50	11.50	41.52	12.48
... ...	,, ,,	,,	Bark, young branches	25.50	15.72	44.38	14.40
... ...	,, ,,	,,	Scrapings, old bark	6.27	3.00	78.62	12.11
... ...	Brugiera gymnorrhiza	,,	Bark, branch	41.76	9.04	35.41	13.79
... ...	,, ,,	,,	Bark, stem	45.04	10.66	32.55	11.75
... ...	,, ,,	,,	Scrapings	7.50	4.33	74.45	13.72
... ...	Ceriops candolleana	,,	Bark, stem	35.00	12.77	41.65	10.58
... ...	,, ,,	,,	Bark, branch	34.82	10.18	43.11	11.89
... ...	,, ,,	,,	Scrapings, stem	14.60	11.63	64.99	8.78
... ...	,, ,,	,,	Scrapings, branch	13.23	10.33	66.83	9.61
... ...	Not stated	Portuguese East Africa	Whole bark	23.30	9.10	57.71	9.89
... ...	,,	,, ,,	,,	28.30	10.60	49.80	11.30
... ...	,,	,, ,,	,,	41.76	7.20	37.51	13.53
... ...	,,	Gambia	,,	25.70	12.40	51.10	10.80
... ...	Brugiera Rheedii	Queensland	Bark	19.48	...	42.61	...

Consequently, leather tanned with the material has a dark red colour, and is therefore rarely used alone, except, perhaps, by Chinese native tanners. In addition, mangrove tanned leather is inclined to be brittle, but when used with other tanning materials gives quite a good leather. As regards the extraction of the bark, the tannin appears to be easily washed out, and Blockey gives 90° C. as the maximum temperature required, while even at 50°-60° C. almost all of the tannin is extracted, with the additional advantage of only 70-87 per cent. of the colour.

Mexican Sumach.

This material is used in Mexico for tanning, and is obtained by grinding the leaves of *Rhus aromatica* (Ait.) and *R. copallina* (Linn.). According to Norton, the material contains about 13 per cent. of tannin. The leaves of the young fustic (*R. cotinus*) is also used to a limited extent, and contain 17 per cent. of tannin.

Mimosa Bark (Wattle bark) (*Acacia*, Sp.).

This very important tanning material—sometimes known by the name of wattle—is obtained from various species of acacia, and contains a catechol tannin. First grown in Australia, it has since (about 1880) been introduced into Africa, where its cultivation has assumed a matter of extreme importance. *A. decurrens* has also been introduced in Ceylon and elsewhere. A large number of authentic samples of the Australian bark have been examined by Blockey, the results of which are given below:—

Botanical Name.	Local Name.	Source.	Tannin.	Non-Tans.	Insol.	Moist.
			Per Cent.	Per Cent.	Per Cent.	Per Cent.
A. pycnantha -	Golden wattle, No. 1	South Australia	49.5	9.4	29.9	11.2
,, -	Golden wattle, No. 2	,,	40.2	9.0	39.6	11.2
A. decurrens -	Sydney green wattle	St Mary (N.S.W.)	41.4	7.9	39.[illegible]	11.5
,, -	Green wattle	Bateman's Bay	38.5	9.1	41.4	11.0
,, -	,,	,,	36.1	7.8	44.5	11.6
,, (v. mollissima) -	Black wattle	...	38.3	4.4	46.2	11.1
A. penninervis -	Hickory bark	Bateman's Bay	37.7	5.2	46.1	11.0
A. binervata -	Black wattle	Cambervarra	30.2	6.7	52.0	11.1
A. dealbata -	Silver wattle	New South Wales	12.2	4.3	71.9	11.6

As will be seen from these analyses, mimosa barks, with the exception of *A. dealbata*, are very rich in tannin, and furthermore it is a light coloured tanning material, a point which no doubt greatly adds to its popularity. In fact, it is of interest to note that Coombes states that the material is so popular in Australia that the supply cannot meet the demand, and considerable quantities have to be imported from Africa.

Turning now to the South African products, the industry in that district has been exhaustively surveyed in a report by C. Williams, Chief Chemist at the School of Agriculture, Cedara, a summary of whose results are given below.

The loss of moisture, which occurs when the green bark is dried by exposure to air, varies from 38-58 per cent., the loss being greater with the thin barks than with the thicker specimens. The actual tannin content of the bark varies with the height above the ground from which it is taken, and the higher up the bark the poorer is the tannin content, thus:—

Age of Tree.	Three Years Old.	Six Years Old.	Nine Years Old.
	Per Cent.	Per Cent.	Per Cent.
Eighth, 6 ft. - -	..	...	...
Seventh, ,, - -	...	27.6	28.9
Sixth, ,, - -	...	28.5	30.1
Fifth, ,, - -	26.8	30.1	31.4
Fourth, ,, - -	29.0	28.7	32.3
Third, ,, - -	31.4	30.4	32.9
Second, ,, - -	30.3	32.9	35.1
Bottom, ,, - -	37.1	36.3	40.6

As regards artificial drying of the bark—a matter of importance to wattle growers—it was found that drying can be carried out at a temperature as high as 150° F. without any destruction of tannin matters, provided such drying is accompanied by efficient ventilation.

Of the varieties cultivated in South Africa, the black wattle, *A. decurrens*, forms the larger proportion, and analyses made at the Imperial Institute of this variety, together with a few others, are given below:—

Botanical Name.	Local Name.	Source.	Tannin.	Non-Tans.	Moist.	Insol.
			Per Cent.	Per Cent.	Per Cent.	Per Cent.
A. decurrens -	Black wattle	Warburg, Natal	35.2	7.3	11.7	45.8
,,	,,	Natal	37.8	9.3	9.5	43.4
,,	,,	,,	35.2	10.3	11.3	43.2
,,	,,	,,	39.8	9.9	9.6	40.7
,,	,,	,,	36.8	10.3	10.4	42.5
,,	Black wattle (chopped)	Cape Colony	35.4	12.0	11.4	41.2
A. pycnantha	...	Cape Colony Dept. of Agric.	40.1	13.0	10.1	36.8
A. saligna -	...		26.4	12.1	11.1	50.4
A. horrida -	Doornbusch	Alexandra, C. Colony	18.3	8.3	11.0	62.4
A. decurrens -	Black wattle (unchopped)	Eastern Conservancy	44.1	7.1	10.9	37.9
...	Mimosa bark	Big Umgagi	18.0	7.5	12.4	62.1
A. decurrens -	5½ years old	Amani, G.E.A.	50.94	8.54	2.95	37.57
,,	,,	,,	39.28	6.29	4.88	49.55
,,	3½ years old	,,	38.12	8.35	10.76	42.77
,,	...	Wilhelmstal, G.E.A.	47.32	7.52	11.02	34.14
,,	10 years old	Kwai, G.E.A.	44.77	8.04	8.75	38.44
A. mollissima	5 years old	Amani, G.E.A.	44.91	5.85	8.71	40.53
,,	,,	,,	38.61	7.27	10.37	43.75
,,	,,	,,	46.78	9.43	9.62	34.17
,,	7 years old	Kwai, G.E.A.	38.14	13.51	8.22	40.13
,,	10 years old	,,	46.39	11.76	6.01	35.84
A. dealbata -	...	Wilhelmstal, G.E.A.	17.42	6.54	11.15	64.89
,,	...	,,	18.51	10.96	12.86	57.67
,,	...	,,	18.48	10.55	11.92	59.05

Mention of Indian grown wattles is made in a report of the Indian Munitions Board by Fraymouth and Pilgrim, who say that those mostly grown in South India are of the species *A. decurrens*, *A. melanoxylon*, and *A. dealbata*, an analysis of the latter showing on the dry bark :—

	Per Cent.
Tannin - - - - -	11.85
Soluble non-tannins - - -	6.89
Insoluble matter - - - -	81.26
	100.00

This compares well with Australian *A. dealbata*, being comparatively poor in tannin, as compared with other species. On the other hand, a sample of *A. decurrens* grown in India showed 42 per cent. tannin, although in an earlier report (1905) by Chatterton, a sample of Nilgiris-grown *A. decurrens* bark yielded only 33.4 per cent. tannin.

Although a very large quantity of mimosa bark is used in this country, a still larger quantity of the prepared extract is favoured by English tanners. The manufacture

of the extract is a matter which has received much attention, and processes are now in operation which yield very good products. In the report by Mr C. Williams already referred to, three extraction processes are mentioned, viz. :—

1. Bilbrough and Frew Process (E.P. 14,405, 1913), similar to the method used for extracting juice from cane sugar. The green bark is passed through a series of crushing rollers, over which a small quantity of water is fed. This enables the recovery of the liquors to be at a high concentration so as to reduce the cost of fuel for evaporation. As the writer is not in possession of fuller details of the process, figures regarding the amount of tannin left in the bark after extraction cannot be given.

2. Patented Process of the Natal Tanning Extract Co., a short description of which by Williams is as follows :—

"The bark is first chopped up finely, and then mechanically conveyed to the leaching vat. This latter is a longitudinal wooden vessel, semicircular in section, and about 50 ft. in length, within which revolve several bronze paddles or propellers for mechanically pushing the chopped bark from one end of the vat to the other. The exit pipe for the infusion is near where fresh bark comes in, and this outlet is so arranged that there is a slow movement of the infusion in the tank in the opposite direction to that of the bark. When the bark reaches the opposite end of the vat, it is mechanically picked up by means of revolving buckets, and finally squeezed through rollers to remove superfluous liquid. To increase the efficiency of the working of the vat, steam coils are placed along the bottom, and the whole vessel is covered in. The whole leaching process is completed in about twenty-four hours."

3. Patented Process of J. A. Tod.

In this method extraction is done in a vacuum whereby it is claimed that a product of better colour is obtained.

It is interesting to note that, owing to the satisfactory colour of the natural extract, no process of bleaching or decolorising has been deemed necessary.

The composition of Natal mimosa extracts is very constant, as is shown by the following figures obtained by the present writer :—

	Per Cent.	Per Cent.	Per Cent.
Tannin	60.9	60.0	61.3
Non-tannins	18.4	20.0	18.4
Insoluble matter	3.8	2.0	2.3
Moisture	16.9	18.0	18.0
	100.0	100.0	100.0

The sugar content of both extract and bark is of interest, as some few years ago a consignment of extract was held up by the Customs Authorities on this account. Some determinations made by the present writer and since published are as under:—

SUGAR CONTENT OF NATAL WATTLE BARK
(*Air-Dried Bark*)

	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Di-saccharoses (as cane sugar)	1.5	2.9	2.4	2.4
Mono-saccharoses (as glucose)	1.8	1.8	1.6	1.9
Total sugars	3.3	4.7	4.0	4.3

SUGAR CONTENT OF NATAL WATTLE EXTRACT
(*Solid Extract*, 20 *per cent. Moisture*)

	Per Cent.	Per Cent.	Per Cent.
Mono-saccharoses	4.4	2.2	3.9
Di-saccharoses	4.2	7.2	3.2
Total sugars	8.6	9.4	7.1

Quite recently a bacterial disease known as ropiness has been studied by Greig-Smith (*Proc. Lin. Soc.*, New South Wales, 1920, p. 52). When mimosa liquors become infected, a slimy growth is formed. It can only occur in weak liquors of under about 2 per cent. tannin strength, and is mainly confined to such liquors as have been prepared from freshly stripped bark, or in old liquors. Preventive measures include steaming or treatment with antiseptics; 3 lbs. of sodium acetate per 1,000 gals. of water will prevent the disease.

Mudus Bark (*Parkia filicoidea*)

A sample of this bark examined at the Imperial Institute gave:—

	Per Cent.
Tannin	12.8
Soluble non-tannins	2.5
Insoluble matter	72.5
Moisture	12.2
	100.0
Ash	6.1

The bark gives a harsh, dark, reddish-brown coloured leather, and in 1906 was valued at £2. 10s. per ton.

Myrobalams (*Terminalia chebula*, Retz.).

The dried fruits of this tree form one of our most valued tanning materials, and on the average contain just over 30 per cent. of a pyrogallol tannin, the amount varying within fairly wide limits according to the district from which they are gathered. According to Perkin the tannin contains cherbulinic acid and a fair proportion of ellagitannin, which on fermentation produces ellagic acid (technically termed bloom).

$C_{28}H_{22}O_{19}$ Cherbulinic acid. $C_{14}H_6O_8$ Ellagic acid.

A very exhaustive examination of Indian myrobalams has been carried out by Parker and Blockey (*J.S.C.I.*, 1903, p. 1181 *et seq.*), who give the following analyses of genuine representative samples:—

District.	Quality.	Tannin.	Soluble Non-Tans.	Insolubles.	Moisture.
		Per Cent.	Per Cent.	Per Cent.	Per Cent.
Bhimley - -	Picked	33.0	13.1	41.7	12.0
" - -	No. 1	38.4	16.1	33.5	12.0
" - -	No. 2	35.2	14.2	38.6	12.0
Rajpore - -	Picked	32.2	13.0	42.8	12.0
" - -	No. 1	35.4	12.1	40.5	12.0
" - -	No. 2	27.6	12.7	47.7	12.0
Jubblepore - -	Picked	28.9	12.7	46.4	12.0
" - -	No. 1	36.5	14.4	37.1	12.0
" - -	No. 2	27.3	14.1	46.6	12.0
Vingorlas - -	...	31.5	9.5	47.0	12.0
Fair Coast, Madras	...	34.8	15.4	37.8	12.0

These investigators also determined the amount of bloom deposited by these varieties by weighing the amount of ellagic acid precipitated by a known amount of the sample. Their results are given in the following table:—

	7 Days.	17 Days.	24 Days.
	Lbs.	Lbs.	Lbs.
Picked Bhimley	0.98	1.16	2.14
Bhimley 1	1.44	1.35	2.79
Bhimley 2	1.72	2.62	4.34
Picked Rajpores	1.55	3.60	5.15
Rajpore 1	0.90	3.54	4.44
Rajpore 2	0.98	3.04	4.02
Picked Jubblepores	3.28	3.43	6.71
Jubblepore 1	6.91	2.95	9.86
Jubblepore 2	4.76	3.63	8.39
Vingorlas	5.15	1.68	6.83
Fair Coast, Madras	1.44	3.37	4.81

As is well known to practical tanners, myrobalams are greatly favoured as an acid-producing body, and are always, or nearly always, used where sour liquors are required. The formation of acid is caused by the fermentation of the sugars contained in the tanning material, myrobalams containing from 3-4 per cent. of sugars. From a practical standpoint the amount of acid produced by myrobalams is of interest, and below is given a table by Parker and Blockey, showing the quantity in terms of acetic acid per 100 lbs. of myrobalams produced from the better known commercial grades:—

LBS. OF ACETIC DEVELOPED FROM 100 LBS. OF MYROBALAMS AFTER STANDING.

	5 Days.	10 Days.	16 Days.	23 Days.	30 Days.
	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.
Picked Bhimley	2.4	3.7	4.1	4.8	5.4
Bhimley 1	3.2	5.1	5.8	6.3	6.4
Bhimley 2	3.2	5.1	5.6	5.6	6.5
Picked Rajpore	2.4	3.9	4.5	4.9	5.4
Rajpore 1	3.1	4.3	4.7	5.3	6.2
Rajpore 2	2.6	3.6	3.9	4.0	4.5
Picked Jubblepore	2.0	2.7	3.2	3.2	3.4
Jubblepore 1	1.9	3.4	3.8	4.1	4.5
Jubblepore 2	3.3	4.2	4.6	4.9	6.3
Vingorlas 1	2.9	3.7	4.4	4.7	5.4
Fair Coast, Madras	2.6	3.4	4.0	4.2	4.8

Paessler (*Collegium*, 1903, p. 369) points out the loss in tannin which takes place when a myrobalam liquor is allowed to stand, but from the practical standpoint it is the opinion of the present author that such losses can be neglected, as there is in almost all liquors a continuous loss of tannin due to fermentation, and the stronger the liquor is, the less the losses through this cause. Thus, Paessler has ascertained that after a period of just over a year a 25° Bé. myrobalam extract lost about 5 per cent. tannin. The point for practical men to bear in mind is, store liquid extracts in as cool a place as possible.

In addition to *Terminalia chebula*, the fruits of other species of Terminalia have been examined with a view to their utilisation as tanning materials. Thus a sample of the fruits of *T. Spekei* tested at the Imperial Institute showed:—

	Per Cent.
Tannin	8.2
Soluble non-tannins	5.6
Insoluble matter	76.5
Moisture	9.7
	100.0

As will be noted, this is not a favourable tanning agent as compared with ordinary myrobalams. Further, this had a dark colour, as distinct from myrobalams, which has comparatively a light colour.

"Sacat Fruit" is the name given to *Terminalia nitens*, and an examination of this fruit from the Philippine Islands, by Gana, gave:—

	Per Cent.
Tannin	19.8
Soluble non-tannins	16.3
Insoluble matter	55.0
Moisture	8.9
	100.0

Also a sample of the bark of *T. velutina* from Uganda gave 13.7 per cent. tannin, 4.6 per cent. non-tannins, and 10 per cent. moisture. The bark from *T. tormentosa* has a tannin content of 10.76 per cent. It happens that the kernels of myrobalams contain practically no tannin, and it might be a paying proposition to separate these by a special process and export the dried fruit alone. The result would be a

material richer in tannin than the ordinary product, and a considerable saving in freightage. A sample of such "crushed" myrobalams examined by the writer contained just 50 per cent. of tannin, as compared with a maximum of 60 per cent. for a properly prepared extract.

"Panga Fruit" is the name given to the fruit of a species of Terminalia derived from Burma (Bulletin, Imp. Inst., 1916, p. 637), and is stated by P. Singh to contain from 20-25 per cent. of tannin and 27-30 per cent. of non-tannin—a very high amount as compared with *T. cherbula.* As regards myrobalams, too, it has been shown (Abstr., Bulletin, Imp. Inst., 1915, p. 318) that the fruit should be picked as soon as it becomes ripe if the maximum amount of tannin is desired.

Some additional analyses of the fruits, etc., of various Terminalia species by Fraymouth and Pilgrim (Report, No. 1) are given below (calculations on dry material):—

Botanical Name.	Common Name.	Tannin.	Soluble Non-Tannins.
		Per Cent.	Per Cent.
T. helerica	Twig bark	10.09	5.99
"	Old bark	6.98	12.74
"	Fruit flesh	25.48	39.02
T. tormentosa	Twig bark	12.30	16.81

N

Native Cherry (*Exocarpus cupressiformis*).

According to Maiden (New South Wales), this bark gives 15.75 per cent. tannin.

Needle Bark (Pine bush bark) (*Hakea leucoptera*).

The needle bark of New South Wales gives a tannin content of 10.99.

O

Oak Bark (*Quercus*, Sp.).

Oak bark can be said to be one of the oldest materials used for the manufacture of leather, but owing to its rather low tannin content (10-14 per cent. of a catechol tannin) and the introduction of other materials and extracts which have proved more convenient for use, it is now getting into disuse to a large extent. Curiously enough, an extract from oak bark has only been prepared to a limited extent, and all the material used has been so in the raw state.

The English oak bark is from *Q. robur* (comprising *Q. pedunculata* (common oak) and *Q. sessiliflora* (durmast or sessile oak)). The information regarding English oak given in a Government leaflet issued at the recent Timber Trades Exhibition, London, is as follows:—

The former, *Q. pedunculata*, is usually found on heavy land at a low elevation, and is distinguished by stalkless, or almost stalkless, leaves and long-stalked acorns, whilst the latter, *Q. sessiliflora*, is more frequent on hillsides and in drier soil. It has stalked leaves and stalkless acorns. The two trees often intermix, and there are examples with intermediate characters, denoting hybrid origin. The timber of the two trees is not separated for commercial purposes.

The common oak usually forms the larger tree, and under the most favourable conditions grows 80-110 ft. high, with a trunk 4-5 ft., or sometimes more, in diameter. Both trees are widely distributed in Europe.

The wood is very distinct by reason of the well-defined rays, which vary a good deal in width, and are easily detected without the aid of a lens. By this means it may be distinguished from sweet chestnut, a similar looking wood, with small and fairly regular medullary rays which can only be seen clearly with the aid of a lens.

The cleanest oakwood and the straightest and longest trunks are obtained by growing the trees close together in woods or forests. Such trees may have clean trunks 20-40 ft. long. The wood is usually straight-grained and free from knots. Trees grown as isolated specimens usually form short, stout trunks.

The tannin content of some species of oak bark grown in England are as follows:—

Botanical Name.	Common Name.	Tannin.
		Per Cent.
Q. tauza - -	...	8
Q. cerris - -	Hairy cupped oak	10
Q. ilex - -	Evergreen oak	10
Q. suber - -	Cork oak	10
Q. ballota - -	...	10
Q. mirbeki -	...	12
Q. coccifera -	...	15
Q. robur - -	English oak bark	12-14

One of the principal kinds of oak bark used in America is that known as Californian tan bark oak (*Q. densiflora*).

The percentage of tannin in this bark is quite high, but varies with its location in the tree, varying from 30 per cent. of tannin and 12.8 per cent. of non-tannins at the base of the tree, to 11 per cent. of tannin and 8.4 per cent. of non-tannins at a height of 80 ft. By cutting down the tree in the proper manner a second crop of sprouts grow from the base, and these sprouts give rise to a second growth of poles or trees, which are commercially profitable to peel within twenty-five to thirty-nine years; the percentage of tannin in the bark of these second growth trees averages 16.2, and the percentage of non-tannins, 9.2.

The wood is excellent for fuel and burns with little smoke and ash, but contains little tannin.

The tannin of the bark is stated to be very valuable for the production of heavy leather. The twigs contain much more tannin than the older wood, so that in extract manufacture, it would be profitable to use them along with the bark.

The bark of the chestnut oak (*Q. prinus*) is also favoured in America, both as a tanning material and as a constituent of tanning extract. According to Brown ("Forest Products"), the average tannin content of *Q. prinus* is 8-14 per cent. of a catechol tannin.

Other varieties of American oaks are given below :—

Botanical Name.	Common Name.	Tannin.
		Per Cent.
Q. alba	White oak	7
Q. relutina	Black oak	6-12
Q. rubra	Red oak	5·5
Q. coccinea	Scarlet oak	7·7

The Santa Cruz oak contains 16-18 per cent. tannin, Siskey oak, 14-16 per cent., and the Sacramento Valley oak, 10-12 per cent.

Two barks belonging to trees of Quercus species from the Philippine Islands have been examined at the Imperial Institute, with the following results :—

Native Name.	Cateban Bark.	Ulayan Bark.
	Per Cent.	Per Cent.
Tannins	10.9	11.0
Soluble non tannins	4.2	3·9
Insoluble matter	74·7	74·9
Moisture	10.2	10.2
	100.0	100.0

Both samples, like the majority of oak barks, give reactions for both pyrogallol and catechol tannins, and, as will be noted from the analytical figures, are similar in composition to ordinary English oak bark of commerce.

The question of Indian oak barks has received considerable attention from Messrs Fraymouth and Pilgrim who deal with them in their admirable report on Indian tanstuffs ("Bulletin," No. 1, 1918, Esociet Research Factory), from which publication the following analyses have been compiled :—

INDIAN OAK BARKS.

(*Results on Dry Barks.*)

Botanical Name.	Common Name.	Tannin.	Non-Tannins.	Insoluble.
		Per Cent.	Per Cent.	Per Cent.
Q. pachyphylla - -	Sungra katus	12.24	10.75	77.01
Q. lineata - - -	Twig bark	10.50	11.04	78.46
" - - -	Mature bark	9.69	11.73	78.58
Q. lamellosa - -	Twig bark	7.86	12.50	79.64
" - -	Mature bark	9.97	17.62	72.41
Q. fenestrata - -	Twig bark	9.48	7.48	83.04
" - -	Mature bark	15.85	8.44	75.71

It will be noted that in the above analyses the ratio of non-tannins to tannins is high as compared with the ratio in English oak barks. There is one exception, *Q. fenestrata*, which, as pointed out by Mr Pilgrim, appears to be the best of the samples examined.

Oakwood (*Quercus*, Sp.).

Whereas oak bark may be said to contain, on the average, 10 per cent. of tannin, the same is not the case with the wood. This only contains about 6 per cent. of a pyrogallol tannin, and is therefore useless as a tanning material. It does, however, form an important raw material for the manufacture of tanning extract as will be gathered below.

The following notes on oakwood and oakwood extract (Slavonian) by Paessler are taken from a translation in the *Leather World.*

Oakwood is not employed directly as a tanning material, but forms the raw material for the manufacture of extract, and since 1883 has been used for this purpose chiefly in Slavonia, and also in France and North America.

Wood from young oaks contains very little tannin, a sample from an eighteen-year old tree giving only 1.5 per cent. tannin and 3.1 per cent. non-tannins, of which 1.6 was glucose (the moisture being 14.5 per cent.). It has been suggested that the younger trees should not be stripped, but the whole wood and bark be used for extract making. This, however, does not improve matters at all, especially as the wood forms

from 85-90 per cent. of the total material. With regard to the older oak trees, Henry has made investigations on the wood from a ninety-year old tree with the following results, based on a moisture content of 14.5 per cent.:—

	Lower Part, 50 cm. Diameter.	Upper Part, 33 cm. Diameter.
Sapwood (11-15 year rings) -	1.0 per cent. tan.	0.9 per cent. tan.
External layer (20 year rings) -	7.8 "	5.4 "
Middle layer (20 year rings) -	6.6 "	4.6 "
Inner layer (20-35 year rings) -	6.7 "	4.8 "

Age has, therefore, considerable influence on the tannin content of the wood, and in general can be said to increase with the age, although cases are known of old wood being low in tannins. Thus in one instance quoted, the heartwood of a thirty-eight year old tree showed only 2.9 per cent. tannins.

Below are given some analyses of various woods of known age; in these cases, however, it includes everything, no separation of the sapwood, etc., being made:—

Age - - -	44	70	70	70	71	72
Diameter in cm. -	14	21	19	23	33	18
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Tannin - - -	8.0	5.5	6.8	7.0	7.0	6.5
Non-tannins - -	1.5	1.5	1.7	1.5	2.0	2.0
Glucose - - -	0.4	0.3	0.3	0.3	0.4	0.3
Cane sugar - - -	0.2	0.1	0.1	0.1	0.2	0.2

For extract manufacture the wood should contain from 5 per cent. upwards of tannin, a lower percentage than this not being considered profitable. A 9 per cent. tannin content is only rarely met with, and is an exception. Stumps, on account of their high tannin figure, are valued for extract making.

The tannin of oakwood is very sensitive to temperatures above 100° C., when it decomposes in notable quantities. Eitner treated oakwood under pressures of 1, 2, 4, and 6 atmospheres at temperatures of 100°, 121°, 143°, and 158° C.

respectively, and the results of such extractions are shown in the following table:—

Atmospheric pressure	1	2	4	6
Temperature, ° C	100°	121°	143°	158°
	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Tannins	6.4	6.5	5.5	2.6
Non-tannins	3.3	4.5	18.1	22.2
Total solubles	9.7	11.0	23.6	24.8

It will be noted that the total solubles increase with pressure and temperature, but such is not due to better extraction of tannin, but to the solution of more non-tannin matters. There appears to be no advantage in extracting the wood under pressure, as although there is certainly a bigger yield of extract the quality of the product is poor.

Paessler has also made extraction experiments under pressure with an old oakwood, extracting also under ordinary atmospheric pressure. The results tabulated below are calculated to a moisture content of the original wood of 14.5 per cent.

Hours' extraction	...	1	2	1	1
Pressure in atmospheres	1	2	2	4	6
Temperature, ° C.	100°	121°	121°	143°	158°
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Tannin	7.7	7.5	8.0	6.7	5.8
Non-tannins	3.3	4.9	6.6	11.6	18.7
Total solubles	11.0	12.4	14.6	18.3	24.5
Glucose	1.0	1.1	1.4	2.2	6.0
Cane sugar	0.3	0.6	1.3	4.2	8.3
Total sugars	1.3	1.7	2.7	6.4	14.3

Here again it is observed that at temperatures above 100° C. more solubles are obtained, but a part of the tannin is decomposed, while at still higher temperatures there is obtained by hydrolysis notable quantities of both glucose and cane sugar.

In the manufacture of oakwood extract, the chopped

wood is extracted with water at a temperature of 90°-95° C., the heating being effected by means of steam pipes under the false bottom of the vat, the contents of which are agitated by the injection of steam. To prevent oxidation, etc., the vats are provided with suitable covers. A series of vats may consist of from six to ten vats, each having a capacity of 26 cubic metres, and capable of holding 8,000 kilos of wood and 20 cubic metres of water, the proportion of wood to water being 1 : 2½. The density of the liquor after the extraction will depend upon the tannin content of the wood, and will be from 2°-2¾° Bé. The time between the filling of the vat and the discharge of the spent tannin is somewhere about thirty-six hours.

The liquor is next clarified, this process being partly mechanical in character, *i.e.*, the settling out of the solid particles, and partly chemical, this latter involving the use of precipitants. As precipitants lead salts are sometimes used, while the Gondolo process, using ox blood, is also favoured. In using the latter process a solution of blood-albumen is frequently used instead of the ordinary blood.

In clarifying, the liquor is cooled down to 40° C., the albumen solution added, and the whole heated up by steam to 60° C. and stirred with a mechanical stirrer. After precipitation, the liquor is allowed to settle for six hours, when, by means of specially placed taps, the clear liquor is run off. The residual sludge is then passed through a filter-press to recover and liquor, and the cake afterwards used as a fertiliser.

Oak extract of 25° Bé. has the following composition (analysed by the shake method): Tannin 24.5 per cent., non-tannins 15 per cent., insolubles 0.5 per cent., water 60 per cent., glucose 3.8 per cent., cane sugar 2.2 per cent., total ash 1.8 per cent.

The carbohydrate content of oak extract has been investigated by Jedlicka, who, in addition to finding from 3.5-5.3 per cent. of glucose, also found 0.6-1 per cent. of galactose. In the hydrolysed solution was found xylose and arabinose. Jedlicka also examined the acids present in both wood and extract, and found in a 25° Bé. extract 0.2-0.3 per cent. of free acetic acid and a further 0.5-1 per cent. in a combined form. Oak extract also contains calcium oxalate.

In the concentration of oakwood liquors a certain amount of acetic acid is produced, and 20-25 kilos of acid in the form of the lime-salt have been obtained as a by-product in the extraction of ten tons of wood. This also includes a small quantity of formic acid. Thuau has made comparative ex-

periments on extraction in open vats and under pressure, extracts prepared having the following composition :—

	Open Vat.	Under Pressure.
	Per Cent.	Per Cent.
Tannin - - - - - -	31.5	26.0
Soluble non-tannins - -	8.5	13.5
Insoluble matter - - -	0.0	0.5
Moisture - - - - -	60.0	60.0
	100.0	100.0
Non-tannins per 100 tannins -	27	52

showing that by pressure extraction more non-tannins are extracted and a poorer extract formed.

Adulteration of oakwood extract is not a very common practice, and even the addition of another extract, such as chestnut extract, is very rarely met with. This latter method of adulteration can be detected by the lead acetate test as devised by Stiasny. 5 c.c. of the tannin solution of analytical strength is treated with 10 c.c. of 10 per cent. acetic acid and 5 c.c. of 10 per cent. lead acetate solution The precipitate is filtered off and the filtrate tested with 10 drops of 10 per cent. iron alum solution and about ½ gm. of solid sodium acetate, taking care not to shake the contents of the test tube. In the presence of chestnut or myrobalams a bluish-violet colour will be formed, while in the event of the absence of these two, no definite colour will form.

Even this test is not infallible, and must be applied with a certain amount of discretion, Jedlicka, for example, having found certain chestnut extracts which do not give a coloration, and on the other hand a pure Slavonian oak extract which did.

Some experiments on the loss of tannin which takes place when an oak liquor is allowed to stand are of interest, and a table of results with a 2° Bé. liquor are given below :—

		6 Days.	18 Days.	30 Days.	60 Days.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Tannin - -	2.07	2.05	1.97	1.85	1.71
Non-tannins - -	0.93	0.93	0.91	0.70	0.49
Insolubles - -	0.00	0.00	0.01	0.14	0.22

These figures show that the tannin content is lowered by the formation of insolubles, and the non-tannins reduced by fermentation. It is mentioned that fermentation in the extract can be prevented by an addition of either 0.3-0.4 per cent. of sodium bisulphite, 0.1 per cent. phenol, or 0.3 per cent. of sodium fluoride.

Osage Orange (Bois d'arc: Aurantine) (*Toxylon pomiferum*, Raf.).

This comparatively new introduction to the list of tanning materials is more in the nature of a dyeing than a tanning agent, and has for some considerable time been used locally in Texas. It is also grown to a small extent in Jamaica. Chemically it is similar to old fustic, containing morin and maclurin. An extract of osage orange wood is marketed under the trade name of Aurantine, its use in tanning being covered by the patent of S. Saxe (U.S.P. 1,297,255).

According to this specification, osage orange wood extract used alone gives a tough strong leather; but when blended with other tanning extracts, it materially improves the leather in respect to strength, toughness, and colour. Other tanning extracts suitable for blending with osage orange wood extract are chestnut, quebracho, oak, hemlock, mangrove, cutch, etc.

It would appear, therefore, to act as a combined tanning and "bleaching" agent, this latter being a feature pointed out by the patentee, thus: "It is found, however, that not only is the strength and toughness of the resultant leather improved, but that the colour is also brightened to such an extent as to render it possible, unless especially light coloured leather is desired, to omit the usual acid-alkali bleaching treatment, which ordinarily follows the treatment in the drum."[1]

The composition of osage orange extract of a sp. gr. 1.255 is given by Saxe as follows:—

	Per Cent.
Tannin	40.06
Soluble non-tannins	12.13
Insoluble matter	3.69
Moisture	44.12
	100.00

[1] *J.A.L.C.A.*, 1915, p. 347.

P

Palmetto (Cabbage palmetto) (*Sabal palmetto*).

An extract prepared from the roots of this American plant has long been used by tanners in the States. The roots are said to contain about 10 per cent. of tannin.

An early analysis by Eitner gave the following:—

	Per Cent.
Tannin	18.01
Soluble non-tannins	20.06
Insoluble matter	2.71
Moisture	49.96
Ash	9.26
	100.00

Later analyses show a much higher tannin content, and the brand made by the Florida Extract Co. is stated to contain tannin 25.9, soluble non-tannins 10.31, moisture 52.94 per cent., and ash 11.09 per cent. Eitner considers it to give a hard, brittle leather when used alone, but in conjunction with other extracts or tanning materials it can be made to produce good sole leather, but even in this instance it should be used with the final liquors only.

Pimenta Leaves (*Pimenta officinalis*).

The possibilities of these leaves, the source of pimento leaf oil, as a tanning material have been investigated at the Imperial Institute.[1] The leaves yield 2.9 per cent. of the essential oil on steam distillation, and in view of the fact that tannin is also present, it was thought that such might be put to profitable use. On examination 14.0 per cent. of tannin and 7.9 per cent. soluble non-tannins were found, the colour of ½ per cent. tannin solution being 9.2 red and 33.9 yellow. Leather tanned with the leaves was pale brown, firm, and of fairly good texture. After extraction of the oil, the residue could be transferred to extraction vessels and leached with hot water. Extract for local use could thus be prepared, but unless large quantities of the leaves are available, export work could not be considered, owing to the high cost of the plant, etc., required for concentration.

[1] Bulletin, Imp. Inst., 1919, p. 299.

Pine, Long-Leaved (Chir pine, Cheer pine, Emodi pine) (*Pinus longifolia*, Roxb.).

The bark of this tree—grown in Japan, where it is used for tanning—has been shown by Trimble to contain 12.9 per cent. of tannin, with a moisture content of 11.75 per cent.

Pine Twigs.

An endeavour has been made in Germany to manufacture a tanning extract from pine twigs and pine refuse. Such an extract is best mixed with a material like quebracho, on account of the high amount of non-tannins present.

Analyses by von Schroeder show the following results :—

	Tannin.	Sugars.
	Per Cent	Per Cent.
Twigs with needles from thirty year old tree	7.03	4.53
Twigs with needles from eighty year old tree	6.10	4.11
From another eighty year old tree - -	5.22	4.08
Top twigs (1 cm. large) from eighty year old tree	4.37	4.59

Pines, Australian.

The composition of Australian pines has been the subject of an investigation by Smith (*J.S.C.I.*, 1911, 1353 *et seq.*), who gives the following figures for air-dried materials :—

NATURAL ORDER, CONIFERÆ; GENERA, CALLITRIS.

Botanical Name.	Common Name.	Collected.	Tannin.
			Per Cent.
Callitris calarata - -	Black pine	June	30.9
" - -	"	May	31.2
" - -	"	July	25.2
" - -	"	March	19.0
C. arenosa - - -		June	15.1
C. glauca - - -	White pine	March	14.6
" - - -	"	April	14.6
C. tasmanica -	...	...	13.3
C. propinqua - -	...	...	12.6
C. gracilis - - -	...	...	12.3
C. intratropica - -	...	...	10.7

In manufacturing tanning extract from pine bark it has been found advantageous to first remove the resins present by extracting the material with a solvent boiling at about 100° C. (Bruml and Silberberger, G.P. 306,529, 1916).

Pistachia atlantica, Desf.

A sample of the leaves of this tree from Libia, and examined by F. V-Lutati, gave the following figures:—

	Per Cent.
Tannin - - - - -	19.74
Soluble non-tannins - - -	21.12

The tannin belongs to the pyrogallol group.

Pistacia Galls (*P. mutica*, Fisch, var. *cabulica*).

These galls, used in Baluchistan for dyeing, have been examined by Hooper, but from the results obtained they do not present a very rich source of tannin:—

	Leaves.	Galls.
	Per Cent.	Per Cent.
Moisture - - - -	7.25	6.85
Resin and wax - -	7.40	10.57
Tannin - - - - -	12.85	15.61
Soluble non-tannins - -	18.88	21.64
Proteins - - - -	9.18	5.50
Fibre - - - -	9.50	10.32

Pomegranate (*Punica granatum*).

The bark of this tree has been said to contain 18 per cent. of tannin, and the shell of the fruit 22 per cent. It is used in Morocco for dyeing yellow shades in conjunction with alum.

FIG. 1.—The Quebracho Tree.

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Q

Quadong (see Blue Fig, p. 16).

Quajacan (see Guyacan, p. 30).

Quebracho (*Quebrachia lorentzii*, Griseb.).

Quebracho extract to-day occupies an important place in the tanning industry, and a short description of the quebracho tree and a general idea of the manufacture of the extract and the part it plays in the tanneries might perhaps provide interesting reading.

The word "quebracho" is a contraction of the two Spanish words *quebra hacha* (axe breaker), and the tree is so named on account of the excessive hardness of its wood.

The tree, which only grows in certain regions of South America, belongs to the oak family, and can be subdivided into three known species:—

The Quebracho Blanco.
The Quebracho Colorado Chaqueño.
The Quebracho Colorado Santiagueño.

The first of these is not exploited to any large extent, on account of the low percentage of tannin and its being too soft to be classed as a hardwood.

The Quebracho Colorado tree is an evergreen, the dark green leaves, like those of the holly tree, ending in sharp points. The leaf of the Chaqueño is isolated, whilst on the Santiagueño it grows in bunches.

The Quebracho Chaqueño is far richer in tannin, containing about 21 per cent. of a catechol tannin as against 12 per cent. in the case of the Santiagueño. On the other hand, the latter grows to a greater size, and is even harder than the Chaqueño.

Both classes of trees are slow growing—in exceptional cases they reach a height of about 60 ft. with a diameter of one metre or more. The average tree is, however, smaller, and does not reach half this height, the trunk

generally measuring 15-20 ft. from the root to the branches. It is estimated that it takes about one hundred years for a tree to grow to maturity.

The quebracho tree is to a great extent a solitaire, and is found dotted here and there; but in the richest forests, that is to say, in the Province of Santa Fé and Gobernacion del Chaco (Argentina), it grows in more or less close formation, at the rate of about twenty trees to the hectare. The heart of the tree contains the tanning material, and the bark (with about 4-5 per cent. tannin) and outer rim are removed and discarded as waste, or used as fuel.

An average analysis of the heartwood, quoted by Paessler, is as follows:—

	Per Cent.
Tannin	17.5
Soluble non-tannins	2.5
Insoluble matter	65.5
Moisture	14.5
	100.0
Glucose	0.2
Cane sugar	0.2

This appears to be on the low side, as the heartwood usually contains at least 20 per cent. of tannin, as shown by Norton in America, thus:—

	Per Cent.
Tannin	28.2
Soluble non-tannins	2.1
Insoluble matter	57.85
Moisture	11.85
	100.00

The sapwood is very poor in tannin, and as a rule only about 3 per cent. is present.

Regarding other constituents, Perkin and Gunnell have isolated ellagic acid and the yellow colouring matter fisetin.

The inception of the quebracho industry in the domain of tanning dates back to the year 1878. In the early seventies of the nineteenth century, a workman employed in some tannery noticed the coloration of the water in which some quebracho sawdust was lying, and thought it might contain some tannin. Experiments were made

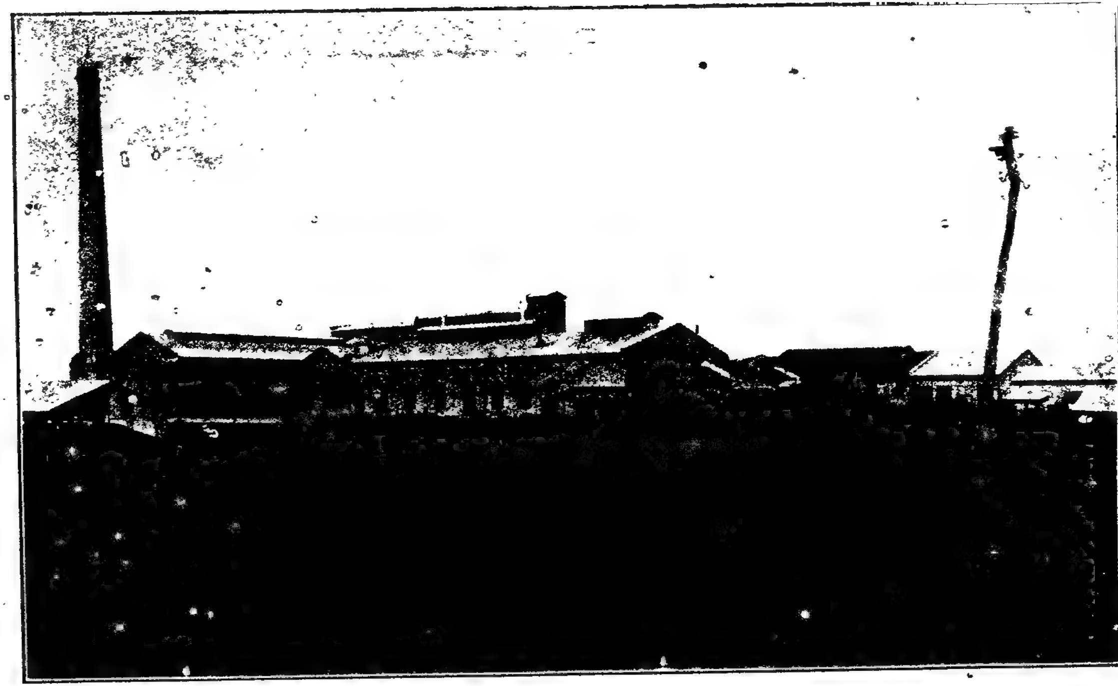

FIG. 2.—Quebracho Extract Factory, Villa Ana (Forestal).

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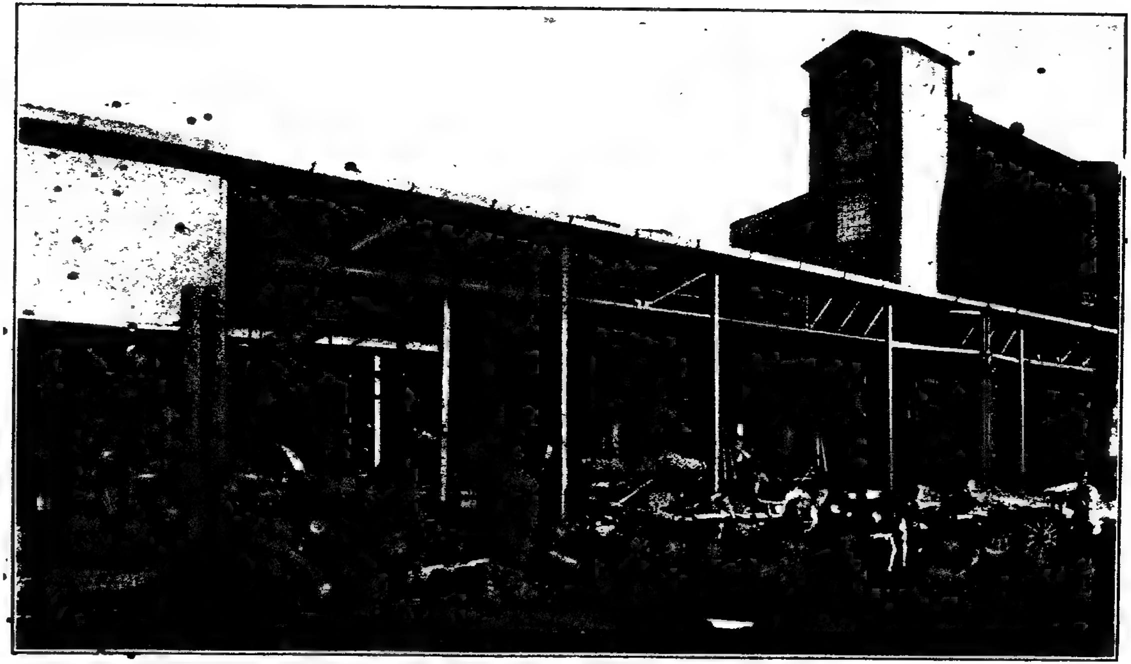

FIG. 3.—Series of Chippers, Villa Ana Factory (Forestal).

To face page 75.

and proved conclusive, and samples were sent in 1872 to Havre and Hamburg.

At first the wood was sent to Europe and later to the United States for the purpose of extracting the tannin therefrom, but afterwards, concurrently with the expanding production of European-made quebracho extract, manufactories for the same purpose were established in Argentina and Paraguay.

The transport of the logs destined either for dispatch to other countries or for local factories for the manufacture of extract presents at times great difficulties, particularly during wet seasons, when the forests become swamped. The trees are felled by native gangs, the branches are severed from the trunk, and the bark and soft outer shell removed. The logs are then carted by waggons drawn by oxen to the light railway connecting with the factory or with the main line. At the factory the wood is conveyed to the chipper, which reduces the log into chips of somewhat coarser nature than ordinary sawdust. The chips are then put into diffusers, three or four of which are connected with one another, and water is added. In the diffusers the water and chips are boiled, and the solution is forced from one diffuser into the other by means of steam pressure, so that the solution from the first diffuser comes into contact with fresh chips in the second, till the solution has passed through the last diffuser. From this latter one it is conveyed to closed depositing tanks, where the evaporation of the water is hastened through vacuum. From these receptacles it is allowed to fall through a slot, in the form of a softish coil, into moulds. In these it solidifies into a crystalline-like solid of a dark red semi-transparent nature, containing from 18-20 per cent. of moisture.

Ordinary quebracho extract as it comes to the market is guaranteed to contain from 63-67 per cent. of tannin, and this standard is well maintained. Soluble quebracho extract is prepared by chemically treating the liquor with sulphites, whereby the phlobaphenes are rendered soluble and do not precipitate when the extract is made up ready for tanning. The solid "soluble" extract known as "Crown" contains 64-68 per cent. of tannin. This process was invented by two Italian chemists, Lepitit and Tagliani, and is aptly described in a paper read by Mr Klepstein in New York, and published in the *Journal Society Chemical Industry*, from which the following abstract is taken:—

"Messrs Lepitit and Tagliani, after long experimenting,

discovered that the sulphurous salts of the alkali metals such as sodium sulphite, bisulphite or hydrosulphite, would so perfectly dissolve the reds of quebracho extract as to keep them soluble, not only in cold water, but in the acid liquor of the tannin vat. They found also that these salts so acted on the soluble tannins of quebracho extract as to prevent their precipitation in sour liquors; in short, they found that by treating quebracho extract with sodium bisulphite or other sulphites under suitable conditions, all loss of soluble tannin was prevented and all the insoluble or difficultly soluble tannins were made available by solution.

"The application of this discovery to quebracho extract eliminated all of its objectionable properties; made its use possible under all tanning conditions and in combination with the sour liquors of all other tanning extracts, thereby adding fully 25 per cent. to its value by saving and utilising the tannins which had previously been precipitated and thrown away. In fact, it is not going too far to characterise this discovery as one of the most important ever made affecting the leather industry.

"Their success with quebracho led the inventors to try the same treatment on other tanning extracts. To their surprise they found exactly opposite results.

"They found that the sulphite treatment has no good effect on chestnut extract and mimosa bark extract, their tannins remaining practically unaltered. It decomposed and partially precipitated the extracts of oak bark, sumac, valonea, myrobalams, and pine bark. After most thorough experimenting they found quebracho extract to be the only one employed in tanning that is practically benefited by treatment with the salts of sulphurous acid."

Quebracho extract is among the quickest tanning materials known, tanning leather in about one-third of the time required with ordinary oak bark, and gives great weight to the leather, thus making it specially valuable for the tanning of sole leather. The illustrations accompanying this section were kindly supplied by the Forestal Land Timber, and Railways Co. Ltd., 149 Leadenhall Street London, E.C., who are the largest manufacturers of ordinary quebracho extract and the sole makers of "Crown" solid soluble quebracho extract.

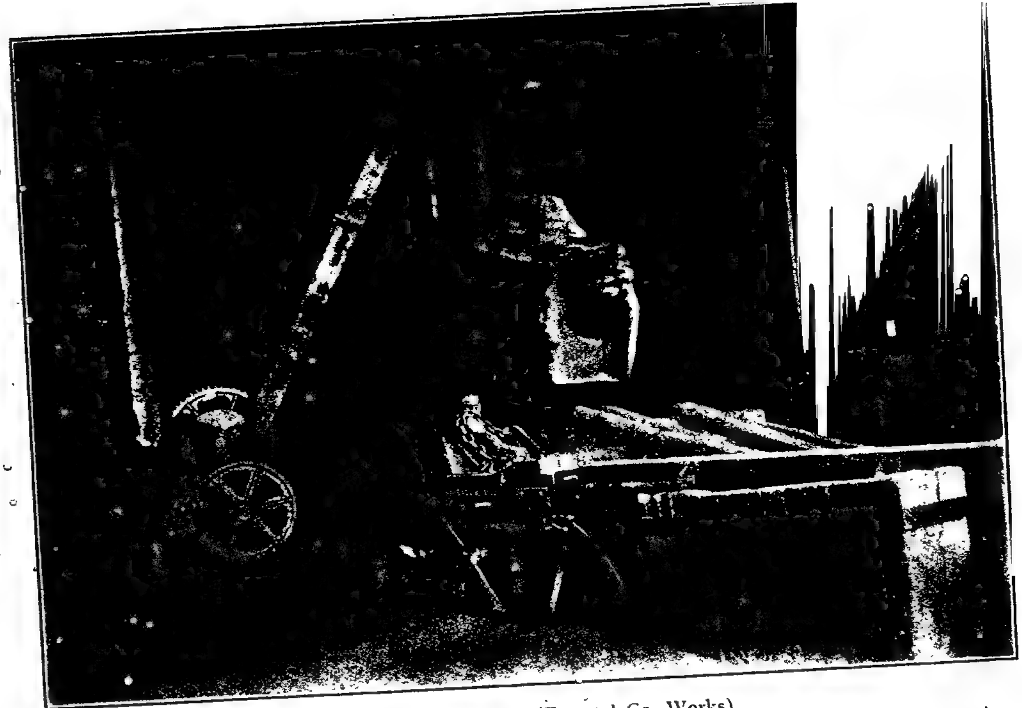

FIG. 4.—Log Chipper (Forestal Co. Works).

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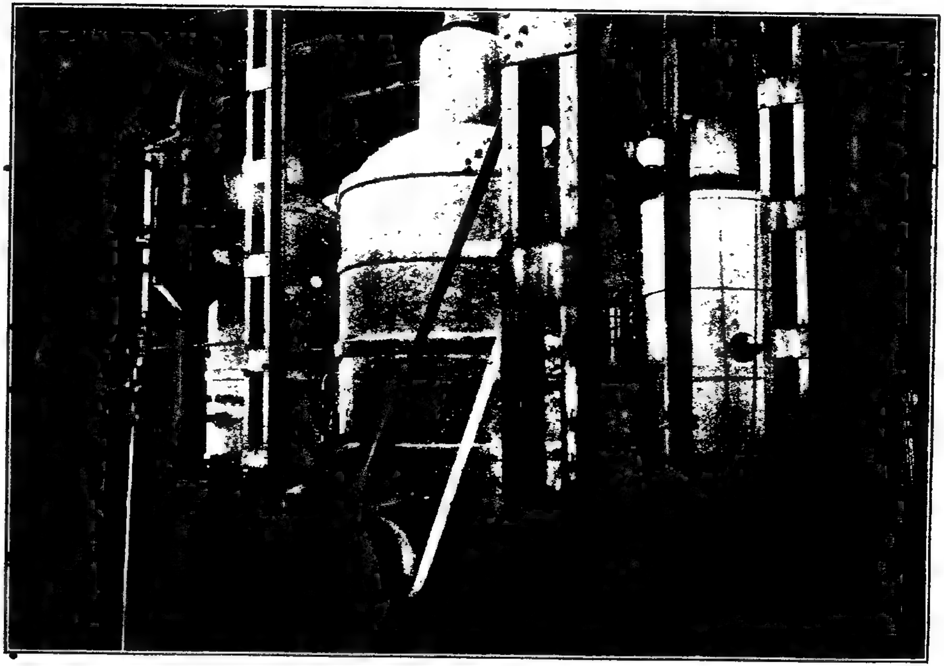

FIG 5.—Evaporators at Villa Ana Factory (Forestal).

Composition of Quebracho Extract.

	Ordinary.		"Crown."	
	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Tannin	66.8	65.8	66.7	67.9
Soluble non-tannins	7.2	9.2	12.6	12.8
Insoluble matter	6.0	6.5	0.0	0.0
Moisture	20.0	18.5	20.7	19.3
	100.0	100.0	100.0	100.0

A note might be made here of an inferior type of quebracho—*Aspidosperma quebracho blanco,* Schlecht—belonging to a different family to the true quebracho. Norton gives the following figures for this "white quebracho":—

Leaves	27 per cent. tannin.
Wood	3 "
Bark	4 "

S

Sal Bark (*Shorea robusta*).

This bark is used in India as a tanning material, while the timber from the tree is said to be one of the most durable of Indian woods. The bark contains 6-9 per cent. of tannin, as shown by the following analyses :—

	1.	2.
	Per Cent.	Per Cent.
Tannin	9.31	6.6
Soluble non-tannins	7.47	8.3
Insoluble matter	83.22	78.6
Moisture	...	6.5
	100.00	100.0

It will be seen that the bark is not particularly rich in tannin, and the question of increasing the tannin content by a process of fibre removal has been carefully studied by Fraymouth in India. His process consists in passing the bark through a disintegrator, and the dust driven into a settling chamber by means of a fan. The result is a powder richer in tannin than the original matter, as is indicated by this chemist from his following analyses :—

	Concentrate.	Fibre.
	Per Cent.	Per Cent.
Tannin	12.33	3.11
Soluble non-tannins	8.42	4.09
Insoluble matter	79.25	92.80
Moisture	...	...
	100.00	100.00

In addition to tannin, the bark also contains a large proportion of oxalates, the recovery on a commercial scale

from which being the subject of a patent granted to Messrs Allen Bros. Ltd. and C. F. Cross, from which it might be gathered that the production of oxalic acid from the spent bark would prove a profitable side-line. The process, in outline, is as follows: The bark from which the tannin has been leached is extracted with a cold 10 per cent. solution of hydrochloric acid for three hours, and the acid liquor concentrated. Lime is then added to precipitate the oxalic acid in the form of calcium oxalate. This is subsequently separated and treated with sulphuric acid to liberate free oxalic acid, which is allowed to crystallise out.

The leaves of *S. robusta* also contain tannin, but, as will be observed below, the relation of non-tannins to tannins is on the high side :—

	Young Leaves.	Mixed Leaves.	Mixed Leaves.
	Per Cent.	Per Cent.	Per Cent.
Tannin	19.85	7.64	8.28
Soluble non-tannins	18.90	16.37	17.25
Insoluble matter	61.25	75.99	74.47
Moisture	..	...	...
	100.00	100.00	100.00

A sample of mixed leaves and twigs extracted with cold water gave 10.56 per cent. of tannin on the dry material, which represented about 41 per cent. of the total tannin present.

As sal bark gives alone a tough leather with a rather reddish tint, it has been found by Fraymouth and Pilgrim that, for local use in India, one-third sal with one-third each of gothar and karunda leaves give the best practical results.

Salai Bark (*Boswellia serrata*, Roxb.).

This tree, according to a report by the Imperial Institute (Bulletin, 1915, p. 351), yields a gum resin which is used in India by the natives in the treatment of rheumatism. At the same time the resin yields a turpentine oil on distillation. The bark has been examined by Pilgrim, who finds—on the dry material—13 per cent. of tannin and 21.9 per cent. of non-tannins.

Silver Fir (Himalayan) (*Abies Webbiana*, Loudon).

The only analysis published is by Trimble, showing a tannin content of 6.9 per cent. on the air-dried bark.

Snow Bush (*Ceanothus velutinus*).

The leaves of this Californian shrub contain about 17 per cent. of tannin. It is a satisfactory tanning agent, but has no plumping properties.

Spruce, Western.

Samples examined by Benson and Thompson gave the following results:—

	Sawmill Bark.	Sawmill Slab.
	Per Cent.	Per Cent.
Tannin - - - -	5.88	3.69
Soluble non-tannins -	6.42	6.79
Insoluble matter - -	72.47	80.37
Moisture - - - -	15.23	9.15
	100.00	100.00

It is remarked that it is probable that the logs from which the above samples were taken had been floating in water for some time.

Strephonema Kernels.

These West African kernels contain 41.8 per cent. of fat, calculated on dry matter, and the residual meal has been found to contain a fair proportion of tannin. Leather tanned with the material would possess a dark colour, owing to the purplish-red colour of the extract.

An analysis made at the Imperial Institute of the fat-free meal is as follows:—

	Per Cent.
Tannin - - - - - -	30.7
Soluble non-tannins - - -	17.7
Insoluble matter - - -	44.3
Moisture - - - - -	7.3
	100.0
Ash - - - - -	3.3
Colour of 0.5 per cent. tannin solution—	
Red - - - - -	7.4
Yellow - - - - -	15.9

Sulphite Cellulose Extract (Wood pulp extract, Spruce extract, Fichtenholz).

During recent years, large quantities of this material have been used for tanning purposes. Although it contains no tannin (or perhaps traces), it has properties whereby it can convert pelt in leather, and, being of vegetable origin, can be considered in the present book. It is prepared from the waste liquors resulting from the "sulphite" process of paper-making. The following is a reprint from the *Leather World* of an article written by the present author, giving some general information regarding this extract:—

In the process of paper-making, pine wood, etc., is treated under pressure with a chemical (calcium bisulphite), with the result that almost everything except cellulose is dissolved, this being left behind in a very pure condition. Now, up to the time when this liquor was suggested as being useful for tanning purposes, it was usually allowed to run to the drain, being considered useless. At the present time this is, by various processes, worked up to form what we now generally term sulphite cellulose extract.

The method of treating the liquor has been the subject of many patents, both in England and abroad, and to indicate the various processes used, the following are quoted as examples:—

English Patent, No. 18,332 of 1914 (Horrocks and Tullis), states that a tanning extract may be prepared from sulphite cellulose liquors by treatment with some soluble salt, such as magnesium sulphate. The mass which is precipitated is pressed off and dissolved in hot water.

English Patent, No. 24,196 of 1914 (Byrom), is rather more complicated, and says that the concentrated liquors are treated with phenols, amino-compounds, or naphthalenedisulphonic acid, or with mixtures of these, or with the middle oil or heavy oil from the distillation of coal, when a soluble light tanning material will be obtained.

A process introduced by Landmark consists in concentrating the liquors in order to volatilise any sulphur dioxide, and next treating them with soda. The lime is then removed by the addition of a suitable chemical, and the clear liquor decanted off from the precipitate which is formed. This liquor is next evaporated to a thick consistency, to form an extract to be used for tanning purposes.

It is seen, then, that the processes put forward for the utilisation of these waste liquors are very varied. It is almost certain that the tanning properties (if any) of sulphite cellulose

extract are due to a substance, or group of substances, other than actual tannin such as is present in ordinary vegetable tanning materials or extracts. F. H. Small, in the Report of a Commission of the American Leather Chemists' Association (1913), states that no substance with the property of tannin could be isolated from cellulose extract.

This fact is fully borne out by the present writer, who, in making a careful examination of an extract, failed to detect by chemical methods any substance having the reactions of tannin. It is interesting to note that a suggestion as to the possible tanning power of these extracts was put forward by Professor Smithells in a discussion on a paper by Procter and Hirst (*J.S.C.I.*, 1909, p. 293). He remarked that if a substance dissolved out of the wood by calcium bisulphite was of an aldehydic nature, then the resultant extract might have some tanning power by virtue of these aldehydes. Little information, however, is available concerning the constituents of sulphite cellulose extract possessing any tanning properties, and much valuable work could be done in this direction.

With regard to its tanning properties, much diversity of opinion exists. Procter (*J.S.C.I.*, 1909, p. 293, and "Tanners' Year Book," 1909) says that, using this extract alone, it is almost impossible to make anything resembling leather; at the same time it may be used in conjunction with the ordinary tanning materials.

A paper in connection with the blending of abstracts with sulphite cellulose has been published in America (*Jour. Amer. Leath. Chem. Assoc.*, 1911), wherein it is indicated that when cellulose extract is used for blending, a loss of a certain amount of tannin appears to take place, and if more than 30 per cent. of the cellulose extract is used in the mixture, the resulting leather has a tinny feel. This defect is more pronounced as the amount of sulphite cellulose extract is increased. When used alone the leather is very tinny, and the grain harsh, as well as having the appearance of not being thoroughly tanned. Procter mentions also that one disadvantage which appears to render the continued use of cellulose extract in liquors almost impossible is that apparently there collects in the liquors a certain constituent of the cellulose extract which tends to produce a brittle and tender leather.

Dr Parker, at the Eleventh Conference of the I.A.L.T.C., introduced for discussion the value of sulphite cellulose extract, during which it was said that these extracts could be used, but the subject was one which required further investiga-

tion; also that it had been already shown that these extracts have the power of combining with pelt, with the production of leather of a kind.

The present writer has also succeeded in tanning pelt with a sulphite cellulose extract. The appearance of a section of the resulting leather was similar to the ordinary vegetable-tanned material. It was, however, very empty and thin, as well as possessing the drawn grain already referred to. On the other hand, the tinniness spoken of by other investigators was quite absent. In spite of this, it was without doubt that the pelt had been changed from such into a type of leather. Such leather, in the writer's opinion, would be of little value for sole leather purposes.

Dr R. Lepetit ("Tanners' Year Book," 1911) expresses his opinion by saying that "the use of sulphite cellulose will certainly not improve the quality of leather."

Using sulphite cellulose extract alone, Hurt (*Jour. Amer. Leath. Chem. Assoc.*, 1913, p. 80) has evidently obtained far better results than those of the present writer quoted above. In his paper he says that "sulphite liquor properly prepared produces a leather which is stronger than leather which I have ever seen tanned with any other material, shows no signs of decay, and which by actual test has proved to be outlasting both hemlock and oak leathers."

Taking into consideration all the various observations given above, it is certain that cellulose extract will tan; but as the conclusions as to its actual value seem a little diverse, it may be that the quality of the leather is dependent upon the method of manufacture of the extract. This suggestion of the writer's seems feasible in light of the fact that it has been previously shown that to prepare an extract capable of tanning pelt the lime present in the crude liquors must be removed.

Another interesting point is, to what extent and how is the cellulose extract taken up by the pelt? It is understood generally that if used at the commencement of the tanning process, and not in excess, it will combine with the hide substance in such a manner as to be incapable of being washed out by water. On the other hand, if used for filling purposes it is stated to be quite easy of detection in an aqueous extract of the leather.

Loveland, however (*Jour. Amer. Leath. Chem. Assoc.*, 1913), was unable to detect, by chemical means, sulphite cellulose in a leather which had been tanned in a cellulose liquor of 50° Bé. This would certainly show that the material is firmly fixed by the hide substance. Such a conclusion has also been arrived

at independently by Lauffman and Moeller. The latter investigator, has also shown that if hides are tanned with a liquor containing a vegetable tanning material together with sulphite cellulose extract, they exert in the liquor a selective action, using up in the first place the tanning material, and then, if not fully tanned, the sulphite cellulose. If, however, enough of the former is present, very little (if any) absorption of the latter takes place.

Let us now consider for a while the composition of these extracts. To begin with, no tannin is present, although it will be noted from the figures given below of analyses by Eitner (*Gerber*, 1911) that there are present some substances capable of being absorbed by hide powder:—

	Per Cent.	Per Cent.	Per Cent.
Absorbed by hide powder	22.8	22.6	25.8
Soluble non-tannins	27.5	28.2	28.0
Moisture	49.6	49.0	46.2
	99.9	99.8	100.0

An analysis of a sulphite cellulose extract, done by the present writer by the official I.A.L.T.C. method, gave the following results:—

	Per Cent.
Absorbed by hide powder	19.7
Soluble non tannins	38.6
Moisture	41.7
	100.0
Ash (mineral matter)	8.16
Glucose	13.48
Protein matter	0.45

The following figures, by Landmark, show the composition of various sulphite cellulose extracts:—

	Tannin.	Non-Tans.	Insol.	Moist.	Ash.	Sugar.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Pionier extract	25.8	27.4	0.0	46.8	8.5	8.0
Hansa extract (with gambier)	20.0	31.3	0.1	39.6	7.9	11.6
Saxonia (P. Golden & Co.)	24.7	20.1	0.0	55.2	5.3	3.9
Excelsior	16.55	33.86	0.0	49.65	12.16	...
Hoesch	28.39	20.13	4.63	46.85	5.60	...
Muskegon	30.73	19.50	4.63	46.85	2.0	...

Sumach (*Rhus coriaria*).

Without doubt, the ground leaf of the sumach plant is one of the best known of tanning materials, especially among light leather tanners. The bulk of the sumach imported into England comes from Sicily, where its production forms an important industry. Here two varieties are known: mascolino (male sumach) and femminello (female sumach), the former being the most valued for tanning purposes on account of its comparatively high percentage of tannin. A nice, light, dry soil is essential to good cultivation coupled with warmth. Under these conditions it flourishes very well, although in some parts of Sicily it grows quite freely at altitudes of 2,000 ft. above sea level.

The leaves of the plant are gathered usually between July and August, and allowed to dry. They are then ground in specially constructed mills, and the powder subsequently submitted to a purification process termed ventilation. Here the ground leaves are blown by means of a fan into settling rooms, leaving such impurities as sand, iron, etc., behind. This treatment results in a very clean product, a point on which the Italian Government are very particular.

Good commercial sumach appears on the market as a light yellowish-green powder containing approximately 26-27 per cent. of a pyrogallol tannin, although wide limits of variation may be put at from 25-30 per cent. When lower than 25 per cent., adulteration with other leaves is suspected. As adulterants, the following are used: *Pistacia lentiscus*, *Tamarix africana*, and *Ailantus gladulosa*.

	Pistacia Lentiscus.	Tamarix Africana.	Ailantus Gladulosa.
	Per Cent	Per Cent.	Per Cent.
Tanning matter absorbed by hide powder	12.8	9.1	11.2
Non-tanning matter, soluble	20.5	25.3	20.4
Insoluble	58.2	57.6	60.0
Moisture	8.5	8.0	8.4
	100.0	100.0	100.0

Some samples which have been examined by the author gave the following results :—

	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Tannin	26.3	25.8	27.2	27.7
Soluble non-tannins	16.9	17.1	17.4	16.2
Insoluble matter	47.5	46.7	45.6	46.0
Moisture	9.3	10.4	9.8	10.1
	100.0	100.0	100.0	100.0
Ash	6.5	6.9	6.8	7.2
Sand	1.1	0.8	1.2	1.1

Lamb in a very comprehensive article in *Leather World*, 1911, p. 111 *et seq.*, divides the various qualities of sumach into three categories, giving the following typical figures:—

	Fair Quality.	Good Quality.	Excellent Quality.
	Per Cent.	Per Cent.	Per Cent.
Tannin	24.2	26.4	28.9
Soluble non-tannin matter	16.8	17.6	15.7
Insoluble matter	52.0	48.2	47.2
Moisture	7.0	7.8	8.2
	100.0	100.0	100.0
Ash and mineral matter	9.5	8.8	8.0

In badly prepared material, the foreign matter, such as stalk, etc., tends to lower the tannin content, and the following figures by Andreasch quoted by Lamb illustrate this point:—

	Tannin.	Non-Tannins.
	Per Cent.	Per Cent.
Dry raw material	20.70	19.11
	19.00	16.70
After winnowing	24.91	15.75
	24.28	16.67
After ventilation	25.82	16.48
After first grinding	27.28	16.11
After ventilation and second grinding	29.98	16.44
Stem and leaf-veins only	14.70	11.70
	8.30	14.43
	11.53	17.77
Sumach leaf, parenchyma only	23.41	17.17
	29.45	15.89

The tannin present in genuine sumach is of the pyrogallol class and is very mild in character. Incidentally it is readily decomposed when boiled with water, and for this reason the leaves when used in practice are never extracted with boiling water. It appears from work by Parker and Procter that the best temperature for sumach extraction is between 50°-60° C., while if it is boiled for half an hour, at least 25 per cent. of the tannin is destroyed. This is a point to which the attention of tanners is particularly drawn.

R. coriaria contains free gallic acid and the colouring matter myricetin.

The cultivation of various species of sumach has received careful consideration in America, and a few years ago an interesting bulletin was published by the U.S. Department of Agriculture. From this publication are taken the following notes on the cultivation of sumach in that particular country.

Species of sumach grown in North America are:—

White sumach (*R. glabra*, L.).
Dwarf sumach (*R. copallina*, L.).
Staghorn sumach (*R. hirta*, L.).
Fragrant sumach (*R. aromatica*, Ait.).
American smoke tree (*R. cotinoides*, Nutt.).
Jamaica or coral sumach (*R. metopium*, L.).
Poisonous sumach or elder (*R. vernix*, L.).
Poison or three leaf ivy (*R. radicans*, L.).

As indicated by the names the two latter species are poisonous. The first three species seem to be those most favoured, and analyses by Veitch and Rogers show the following results:—

	Tannin in Leaves and Stems.			Tannin in Stalks.		
	Average.	Max.	Min.	Average.	Max.	Min.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Dwarf sumach -	28.95	35.03	19.46	7.77	9.94	5.09
White „ -	25.14	28.08	21.35	6.84	7.30	6.19
Staghorn „ -	27.66	30.59	21.53	7.03	8.09	6.45

Further analyses of American species of sumach by F. A. Blockey (*J.S.C.I.*, 1902) are :—

Botanical Name.	From.	Tanning Matter.	Non-Tanning Matter.	Insol.	Water.	Colour Measurement.	
						Red.	Yellow.
		Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Rhus glabra	Southern States, U.S.A.	24.6	16.5	51.8	7.1	1.3	3.2
R. typhina	Virginia	12 7	15.8	60.4	11.1	3.5	8.0
R. aromatica	U.S.A	12.6	10.1	64.9	12.4	5.9	14.0
R. cotonoides	,,	20.4	12.6	53.3	13.7	3.3	7.3
R. semialata	,,	4.7	8.5	75.3	11.5	22.4	64.0
R. metopium	,,	8.2	13.0	68.5	10.3	...	..

The question of utilising the spent leaves has also been investigated, but there appears to be very little manurial value in this by-product. This is gathered from the fact that commercially extracted leaves and leaf stems with a 5 per cent. moisture content only gave about 1.7 per cent. CaO, K_2O 0.1 per cent. and P_2O_5 0.2 per cent. on chemical analysis. It is pointed out, however, that the organic matter would be useful on land deficient in this soil constituent.

Sumach extract, used largely as a substitute for sumach leaves, is made by extracting the natural material and evaporating the liquors to a sp. gr. of about 1.20-1.22 containing from 26-30 per cent. of tannin.

The quality of sumach extract is particularly dependent upon the method of extraction, and the action of air at an elevated temperature would rapidly cause deterioration in both tannin and colour of this material.

Two examples of yield are given by Dumesny and Noyer in their well-known book; in the first, 43 per cent. of dry extract was obtained by a cold extraction, corresponding to 92 per cent. of 25° Bé. liquid extract. With hot extraction (80°-90° C.) a 78 per cent. yield of 25° Bé. extract was obtained.

In practice, sumach is used very largely by light leather tanners in the manufacture of sheepskin leathers; retanning with sumach is often carried out on several classes of leathers after stripping with borax and washing. Such a retanning helps to clear the grain of the leather and effects a partial bleaching, thus serving as a good ground for the production of light shades.

The barks from several members of Rhus sp. grown in

India have been analysed by Pilgrim and Fraymouth, who find the following tannin contents based on the dry bark :—

R. mysorensis -	Twig bark	18.52 per cent.
R. acuminata -	Bark	9.78 ,,
R. semialata - -	,,	7.84 ,,

Sumach, Indian (*Rhus cotinus*).

Both leaves and bark of Indian sumach contain tannin, the former to the extent of 18-22 per cent. (when collected in the autumn) and the latter from 8-20 per cent

T

Tanskehi Bark.

This is the native name of a New Zealand tanning material containing about 28 per cent. of a rather reddish coloured tannin. It has been proposed to make an extract from the bark in such a manner as to lessen the high amount of reds.

Tea (*Camellia thea*, Linn.).

Although not used to any large extent for tanning purposes, tea contains a fair proportion of tannin. A sample of tea fluff examined by Fraymouth gave 8.38 per cent. of tannin calculated on the dry matter. The colour of a ½ per cent. tan solution is very high. Other analyses, made at the Imperial Institute and published in the Bulletin, are tabulated below :—

	Uganda Tea.	Indian Tea, Average.	China Tea, Average.	East Africa Tea.	Fiji Tea.
	Per Cent.	Per Cent.	Per Cent	Per Cent.	Per Cent.
Moisture	8.05	0.0	0.0	8.6	10 6
Tannin	9.5	9.2	5.2	9.6	7.9
Total extract [1]	36.0	31.7	24.3	33.9	26.2

It will be seen that even if waste tea could be used locally as a tanning agent, the amount of non-tannins substance present is high.

Terra Japonica (see Gambier, p. 27).

Teri Pods (*Cæsalpinia digyna*).

These pods are very rich in tanning matters as will be seen from the following analyses made by the Imperial Institute :—

[1] *A known weight of the sample digested with* 100 *times its weight of boiling water for ten minutes.*

Origin.	Moisture.	On Dry Matter. Tannin.	Non-Tannins.	Ash.
	Per Cent.	Per Cent.	Per Cent	Per Cent.
Burma -	11.07	53.82	15.88	2.28
,, -	10.93	53.86	16.54	3.76
Assam -	11.40	59.89	14.31	1.84
,, -	13.72	45.45	18.95	2.30
Burma -	13.17	59.50	23.10	2.10
,, -	10.8	54.5	18.50	2.78

These analyses are of the pods freed from the hard spherical seeds they contain. Like other tanning "pods" *C. digyna* gives infusions which are subject to rapid fermentation.

It gives a light coloured soft leather similar to divi-divi, and the shade does not materially alter as the result of four weeks' exposure to sunlight.

"**Tizra**" ("Tizra Sumach," "Tezera") (*Rhus pentaphylla*).

This material, found to a large extent in Morocco, contains an appreciable amount of tannin, and is largely used by the Arabs as a tanning material. The leaves apparently are only used in dyeing for the production of yellow shades. Two samples of "tizra" from Morocco examined by the author gave the following results:—

	Roots.	Wood.
	Per Cent.	Per Cent
Tannin -	29.1	23.0
Soluble non-tannins	2.6	3.6
Insoluble matter -	56.6	60.5
Moisture	11.7	12.9
	100.0	100.0
Colour of 0.5 per cent. tannin solution:—		
Red	13.6	8.2
Yellow	27.3	9.5

The tannin in both roots and wood was of the catechol group.

The above analyses represent true *R. pentaphylla*, a

sample of which was kindly identified as such for the author by the Director of Kew Gardens. The manufacture of extract from *R. pentaphylla* has been patented by Marty and Pradon in F.P. 439,784, 1912.

Turwad Bark (Turwar, Avaram, Avla, Awal) (*Cassia auriculata*).

This Indian tanning material has been the subject of extensive investigation by Limaye, Mehd, and Fraymouth and Pilgrim. It is also mentioned in earlier reports on the Indian leather trade by Guthrie and Chatterton.

The tannin present belongs to the catechol group, and appears to be fairly easily extracted by water. Experiments by Mehd on this point gave the following figures :—

Temperature.	Tannin.	Non-Tannins.
Degrees.	Per Cent.	Per Cent.
30-40	15.5	10.0
40-50	16.6	11.2
50-60	19.5	11.8
85-90	22.1	11.2

The tannin content varies from 15-19 per cent., although 20 per cent. has been recorded as being present in the bark taken from the lower part of the plant, which, as pointed out by Limaye, is usually richer in tannin than bark from the upper parts of the plant.

Below are given the composition of a few selected samples and some commercial samples examined by Limaye :—

	Tannin.	Soluble Non-Tans.	Moisture.	Insoluble Matter.
Commercial Samples—	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Poona market	16.8	5.8	7.8	69.6
Bombay market	18.1	7.9	9.6	64.4
Ahmednagar market	14.4	8.9	13.3	63.4
From Palanpur	18.7	6.5	11.6	63.2
From Tandur	17.6	6.1	10.6	65.7
Picked Samples—				
Charoli (3 years) upper	17.90	10.70	8.87	62.53
Charoli (3 years) lower	18.80	10.60	8.85	61.75
Baramati (3 years) upper	18.40	9.90	11.07	60.63
Baramati (3 years) lower	20.9	10.5	10.3	58.3

It may be taken that for the tanning of light leathers intended for bookbinding, turwad bark is not of much use, but for other purposes, especially when used in conjunction with myrobalams, it finds many satisfactory applications.

The colour of leather tanned with turwad is of a light yellowish colour, which is affected by sunlight, turning a reddish shade.

U

Ulmo (*Eucryphia cordifolia*, Cav.).

The bark of this tree is largely used in Chile for tanning. An extract is made and exported mainly to the United States. A sample of such extract, presumably liquid, examined by Paessler, gave 21.9 per cent. tannin and 10.2 per cent. non-tannins. Its great disadvantage is its deep colour, which to some extent resembles that of mangrove.

V

Valonia (*Quercus ægilops*, Linn.).

The valonia of commerce consists of the acorn cups of the Turkish oak, while another variety is obtained from the Greek Archipelago. From investigations made by Parker and Leech (*J.S.C.I.*, 1903, p. 1185) it is clear that the Smyrna variety is to be preferred to the Greek, both from the point of view of tannin content and bloom formation (ellagic acid); but the Greek variety is stronger in acid-forming properties.

The following table of analyses is by Parker and Leech (*loc. cit.*) and shows the composition of—

(1) The whole valonia.
(2) The cup separately.
(3) And the "beard" attached to the outer surface of the cup.

	Tannin.	Non-Tannins.	Insoluble Matter.	Moisture.	Glucose.
Smyrna—	Per Cent.	Per Cent.	Per Cent	Per Cent.	Per Cent.
Valonia	32.43	12.5	43.07	12.0	2.05
Cup	30.99	12.79	44.12	12.0	1.60
Beard	43.61	14.45	29.93	12.0	2.05
Greek—					
Valonia	32.07	12.96	42.97	12.0	1.5
Cup	27.37	12.96	47.71	12.0	1.05
Beard	41.03	13.96	33.01	12.0	1.55

It is known that the best quality Greek valonia is collected during April, and the most inferior grade late in the year, the selections being known as—

(1) April collection—chamada.
(2) September-October collection—rhabdisto
(3) Later, after the rains—charcala.

The latter are very rarely, if ever, used for tanning, owing to their low tannin content.

The formation of bloom is one of the characteristics of valonia, and is a property taken advantage of by sole leather

tanners. It goes to produce a solid, firm leather of satisfactory weight. Parker found that Smyrna valonia gave the highest yield of bloom, and that 75 per cent. of the total was deposited in leather within the first fortnight. In the layers the property of bloom formation is fully appreciated.

As is the case with most tanning materials, successful attempts have been made to manufacture an extract of valonia, and a liquid variety containing about 26 per cent. of tannin is on the market.

The solid extract in powder form is known by the trade name of "Valex." This is manufactured in Smyrna by a particular process and is said to contain from 64-65 per cent. of tannin and 23 per cent. of non-tannins. A careful analysis by Paessler (*Collegium*, 1907, p. 903 *et seq.*) gave :—

	Per Cent.
Tannin	68.0
Non-tannins	24.3
Moisture	7.5
Insolubles	0.2
	100.0

A detailed account of the collection, etc., of valonia appeared in "The Tanners' Year Book" for 1912, while some additional remarks are contained in an article in Bulletin, Imp. Inst., 1912, p. 645.

W

Wattles (see Mimosa, p. 51).

West Indies (Various tanstuffs from).

Apart from other West Indian tanning materials mentioned elsewhere, Sack (*J.S.C.I.*, 1906, p. 436) has examined a few of minor importance and his results are tabulated below:—

			Tannin.	Non-Tannins.	Moisture.
			Per Cent.	Per Cent.	Per Cent
Oemabarklak -	Bigonia inæqualis	Bast	14.0	7.0	...
Krappa -	Carapa guyanensis	„	6.0	5.0	..
..	Cassia florida	Bark	2.5	4.1	58.0
	„	Husk	10.0	...	...
...	„	Seeds	10.0	44.7 oil	

Western Larch (*Larix occidentalis*).

The material has been analysed by Benson and Jones, who give the following figures for the wood and bark:—

	Wood.	Bark.
	Per Cent.	Per Cent.
Tannin - - -	6.7	10.6
Soluble non-tannins -	23.9	6.4
Insoluble matter -	61.6	72.0
Moisture - - -	7.8	11.0
	100.0	100.0

White Birch (see Birch bark, p. 16).

Willow Bark (*Salix*, Sp.).

The bark of the osier (*Salix viminalis*), used in basket-making, contains from 7-10 per cent. of tannin. The tannin contents of other species vary from 2-6 per cent. These barks are largely used in Russia for tanning purposes.

Wood Pulp Extract (see Sulphite cellulose, p. 81).

Y

Yellow Cutch (see Gambier, p. 27).

Yellow Pine (*Pinus ponderosa*).

This wood is largely used for boxmaking, and the sawdust resulting is considered by Benson and Jones as a possible raw material for extract making. Its composition is :—

	Wood.	Bark.
	Per Cent.	Per Cent.
Tannin	8.0	10.9
Soluble non-tannins	8.0	8.3
Insoluble matter	..	76.8
Moisture	.	4.0
		100.0

The bark of *P. abies*, commonly termed pine bark, contains about 11 per cent. of a catechol tannin together with some sugary substances. It is widely used on the Continent in the form of extract.

Yew (*Taxus baccata*).

This bark is rich in tannin, and a sample of Japanese origin was tested by Trimble and found to contain 19.55 per cent. of tannin on the air-dried material.

MINOR TANNING MATERIALS OF LATIN AMERICA.

(Compiled from Special Agents' Bulletin, No. 165, U.S.A., by T. H. Norton.)

Botanical Name.	Native Name.	Tannin.	Origin.	
		Per Cent.		
Rollinia, Sp.	Aratiku gwazu	4.2	Paraguay	Bark
Aspidosperma polyneuron, Muell.	Palo rosa	2.6	,,	,,
Tecoma ipé araliacea	Lapacho	5.0	,,	,,
Apuleia præcox, Mart.	Yhvihrá-perè	10.7	,,	,,
Copaifera lansdorfii, Mart.	Kupaih	16.6	,,	,,
Alchornea triplinervia, Mart.	Tapia gwazu-ih	11.7	,,	,,
Croton succirubrum	Sangre de drago	11.7	,,	,,
Salbergia, Sp.	Yhsapih-ih	5.8	,,	,,
Rheedia brasilinsis	Pakuri	21.6	,,	,,
Ocotea, Sp.	Yhvá-ikâ	10.8	,,	,,
Cabralea, Sp.	Cancharana	5.0	,,	Young bark
Cedrela tubiflora	Cedro	12.6	,,	Bark
Trichilia categua, A. Juss	Kaátiguá pinhtâ	20.5	,,	,,
T. hieronymi, Griseb.	Kaátiguá morôti	23.0	,,	,,
Enterolobium timboüva, Mart.	Limbo	22.3	,,	,,
Inga affinis, D.C.	Inga gwazu	25.8	,,	,,
Peltophorum dubium, Taub.	Yhvrihrá pinhtâ	31.2	,,	,,
Piptademia rigida, Benth.	Kumpaih-râ-pinhtâ	28.2	,,	,,
Britoa fragrantissima	Yhváviro	9.2	,,	,,
Campomanesia guavirá	Yhvavirá	11.6	,,	,,

Eugenia braziliensis, Lam.	Yhvá-poroitih	43.6	,,	,,
,, ,, ,,	,,	11.6	,,	Wood
,, ,, ,,	,,	16.6	,,	Leaves
E. Michellii, Lam.	Nanga pinih gwazu	28.5	,,	Bark
E. pungens, Berg.	Yhvá viyu	10.8	,,	,,
Eugenia, Sp.	Regalito	15.8	,,	,,
,,	Yhvajhay pinhtâ gwazu	28.7	,,	,,
Myrtus edulis	Yhvá mbopı	21.8	,,	,,
Cocos romanzoffiana, Cham.	Pindo	6.6	,,	,,
Allophyllus edulis, Radlk.	Kôkû	10.0	,,	,,
Cupania uraguensis, H. and A.	Kambuatâ	17.5	,,	,,
C. vernalis, Cambess.	Yaguarataih	15.0	,,	,,
Cupania, Sp.	Cedrillo	15.8	,,	,,
Bumelia obtusifolia, R. and S.	Pihkásurembiu	8.4	,,	,,
Piptademia cebil, Griseb.	Red cebil	15-25	Argentine	,,
,, ,, ,,	,,	6-7	,,	Leaves
Acacia cebil, Griseb.	Cebil	8-12	,,	Bark
,,	,,	7 8	,,	Leaves
Mimosa farinosa, Griseb.	...	3.9	,,	Bark
Eugenia jambos, Linn.	...	12.4	Brazil	,,
Persea lingue	Lingue	20-24	Chile	,,
Tecoma pentaphylla	Roble colorado	27	Venezuela	,,
Fuchsia macrostemma	Churco	25	Chile	Root bark
Krameria trianria, Ruiz	Rhatany	38-42	Peru	Root
Acacia cavenia	Espinillo	33	Argentine	Fruit husk

SECTION I

INTRODUCTION

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INTRODUCTION

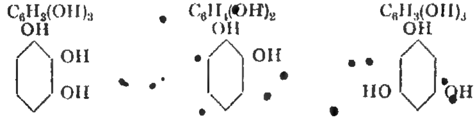
THE tannins are a group of similar astringent substances occurring in various parts of plants, *i.e.*, leaves, bark, wood, roots, etc. Two main properties common to all tannins are :—

(1) Formation of a dark colour (blue-greenish black) with iron salts.

(2) Formation of an insoluble tannin-gelatine compound with solutions of gelatine or glue, this reaction being somewhat similar to the formation of leather by the rendering of hide fibres insoluble in water.

All tannins are not identical in chemical composition, although they are all composed of the elements carbon, hydrogen, and oxygen. Hence they belong to the organic group of chemical compounds, and as on decomposition by appropriate methods they yield phenolic substances, they are classed with the aromatic series. The classification of tannins for technical purposes is based on the decomposition products formed by the action of heat. In the main one of two substances is formed, pyrogallol or catechol, while in some instances phloroglucinol is produced :—

Pyrogallol	*Catechol*	*Phloroglucinol*
$C_6H_3(OH)_3$	$C_6H_4(OH)_2$	$C_6H_3(OH)_3$



It will be noticed that pyrogallol and phloroglucinol have the same formula, but a different arrangement of the hydroxyl groups (OH). Such substances are termed isomeric, and the difference in structural arrangements accounts for the difference in properties of the two substances.

The tannins, then, are divided into two main groups, catechol and pyrogallol tannins.

Catechol Tannins.—Birch bark, oak bark, quebracho, mangrove, ulmo, gambier, mimosa bark, hemlock, mallet bark, lentisco, pine bark.

Pyrogallol Tannins.—Myrobalams, valonia, algarobilla, oakwood, galls, chestnut wood, willow bark, sumach, babool.

Other marked differences, noticeable from the practical standpoint, are:—

Catechol Tannins.—Deposit "reds" or phlobaphenes, and often form but very little acid.

Pyrogallol Tannins.—Liquors of pyrogallol tanning materials deposit a whitish substance, ellagic acid, generally give a fair amount of acid, and produce on the whole rather softer leathers than the catechol tannins.

Hence one sees the point of the present-day mixed tannages, *i.e.*, the use of more than one tanning material in the preparation of liquors. Both "reds" and "bloom" are capable of being absorbed by hide during the tanning process, and have value in giving weight and solidity to the finished leather. The "reds" or phlobaphenes are considered to be anhydrides or oxidation products of tannins, while the "bloom" deposited by the pyrogallol tannins consists of ellagic acid, $C_{14}H_6O_8$. In addition to being formed by fermentation of tannin infusions, ellagic acid can also be prepared by boiling the tannin solution with weak sulphuric acid.

The acid produced by either process can, according to Perkin, be crystallised from pyridine, from which solvent it crystallises with pyridine of crystallisation. It is interesting to note in passing that ellagic acid constituted the alizarin yellow paste of commerce, put on the market by a German concern.

A number of tannins have been isolated in as pure a form as possible and examined by Perkin, Nierenstein, Fischer, and others.

Cherbulinic acid is the name given to the tannin present in myrobalams. On heating for a short time with water, decomposition takes place with the formation of gallic acid, and it is for this reason that, in examining this material in the laboratory, extraction is carried out at as low a temperature as possible. Blockey has shown that

at 50°-60° about 96 per cent. of the total tannin is extracted, and although this writer only indicates a loss of about 2 per cent. after half an hour's boiling, it is more than likely that under works conditions this loss would be considerably increased.

Oak bark contains a tannin to which the name quercitannic acid has been given, while that present in oak wood is termed quercic or quercinic acid, the formula for which is $C_{15}H_{12}O_9$, $2H_2O$.

The tannins in many cases are closely related to the colouring matters with which they are associated, and the separation from which is often a matter of extreme difficulty. For very complete details on this subject, reference should be made to that excellent monograph by Drs Perkin and Everest on "The Natural Organic Colouring Matters."

As might be expected with a simple plant infusion, there are present many substances other than tannin which are collectively termed "non-tannins." Such non-tannins are sugars, colouring matters, nitrogenous matter, gummy matter, etc., and it has been established that the non-tannins play an important rôle in the actual process of leather making. In fact, so much importance is to be attached to these non-tannin substances, that it might be well to recall Professor Procter's remarks on this subject, who said that many non-tannins put in to give solidity would really be found to have tanning properties[1] (Leather Trade Conference, *Leather World*, 1920, p. 1324).

Of the non-tannins, the sugars can be said to take first place from the point of view of practical utility. By fermentation, they give rise to acids (mainly acetic acid and lactic acid) so essential in the early stages of tanning. Incidentally, it is of interest to note that further fermentation may take place and convert some of the acid into alcohol, and the present writer has met with a sumach extract containing appreciable traces of ethyl acetate (an organic compound of alcohol and acetic acid). In all tanning materials there exist certain protein (nitrogenous) substances, and Bennett (*Collegium*, Lond. Edit., 1916, p. 167) considers, rightly, that this nitrogenous matter, or at least the soluble portion of it, acts as a food for the organisms which bring about the acid fermentations. The amount of nitrogen present

[1] It has since been established by Wilson and Kern, that if the soluble non-tannins be evaporated down and then diluted with water, the resultant solution will give a definite reaction for tannin. Hence a conversion of non-tannins into tannin.

in tanning materials has been investigated by Bennett (*loc. cit.*, p. 1), whose results are tabulated below :—

	Per Cent.		Per Cent.
Myrobalams	0.56	Lentisco	1.18
Valonia cup	0.29	Quebracho wood	0.17
Valonia beard	0.34	Quebracho extract	0.126
Natal bark	0.87	Chestnut extract	0.079
Sumach	0.87	Cube gambier	0.45

Other non-tannin constituents are colouring matters, phenolic substances, and mineral salts.

There are other methods of classifying the tannins in addition to that already given. Thus Perkin ("Natural Organic Colouring Matters," p. 413 *et seq.*) divides them as follows, based on purely chemical considerations :—

(1) The depside group.
(2) Diphenyl methylolid group or ellagitannins.
(3) The catechol or phlobatannins.

In the present work, however, the first mentioned and more popular classification has been adhered to.

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